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VOL.
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58/9

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CONTENTS OF VOLUME I

NUMBERS 1/2

Foreword

PERCY STOCKS: Air pollution and cancer mortality in Liverpool Hospital Region and North Wales *page* 1

B. T. COMMINS: Polycyclic hydrocarbons in rural and urban air 14

JOHN J. PHAIR, GEOFFREY C. R. CAREY, ROY J. SHEPHARD and MAURICE L. THOMSON: Some factors in the design, organization and implementation of an air hygiene survey 18

P. A. SHEPPARD: The effect of pollution on radiation in the atmosphere 31

D. P. BENTON, G. A. H. ELTON, E. A. PEACE and R. G. PICKNETT: Coalescence of droplets in aqueous-disperse aerosols 44

A. J. HAAGEN-SMIT and MARGARET F. BRUNELLE: The application of phenolphthalin reagent to atmospheric oxidant analysis 51

P. J. MEADE and F. PASQUILL: A study of the average distribution of pollution around Staythorpe 60

D. H. LUCAS: The atmospheric pollution of cities 71

N. G. STEWART, H. J. GALE and R. N. CROOKS: The atmospheric diffusion of gases discharged from the chimney of the Harwell reactor BEPO 87

H. J. GALE and L. H. J. PEAPLE: A study of the radon content of ground-level air at Harwell 103

J. R. GRAHAM: Smoke pollution and household costs 110

Review Articles:

B. C. ODDIE: Atmospheric chemistry 114

G. NONHEBEL: The technical provisions of the British Clean Air Act 120

Reports of Meetings:

W. STRAUSS: Air pollution and the iron and steel industry 139

A. R. MEETHAM: Air pollution symposium at Cincinnati 143

R. S. SCORER: Atmospheric diffusion and air pollution 145

Book Reviews:

"Particulate Clouds", by H. L. GREEN and W. R. LANE (reviewed by R. S. SCORER) 148

"The Air Pollution Handbook", edited by P. L. MACGILL, F. R. HOLDER and C. ACKLEY (reviewed by R. S. SCORER) 149

"Dust is Dangerous", by C. N. DAVIES (reviewed by D. E. HICKISH) 150

"Kolloquium über meteorologische Probleme der radioaktiven Luftverseuchung" (reviewed by P. A. SHEPPARD) 150

"Natural Aerodynamics", by R. S. SCORER (reviewed by P. J. MEADE) 151

"Les Aerosols", by P. AVY (reviewed by G. A. H. ELTON) 152

"Air Pollution", edited by M. W. THRING (reviewed by MARJORIE CLIFTON) 152

Papers to be published in future issues 154

NUMBER 3

ELLIS F. DARLEY, EDGAR R. STEPHENS, JOHN T. MIDDLETON and PHILIP L. HANST: Oxidant plant damage from ozone–olefin reactions *page* 155

F. T. FOX and L. M. MARSHALL: Application of microdiffusion of organic acids to air analysis 163

MARY O. AMDUR: The physiological response of guinea pigs to atmospheric pollutants 170

B. R. MORTON: The ascent of turbulent forced plumes in a calm atmosphere 184

R. S. SCORER: The behaviour of chimney plumes 198

C. JEHANNO et C. LALLEMANT: Détermination de la pollution de l'air et de l'irradiation au sol, dues au "panache" d'un réacteur en marche normale 221

S. KANNO: The colorimetric determination of sulfur oxides in atmosphere 231

S. KANNO, S. FUKUI, H. IKEDA and Y. ONO: Atmospheric SO_2 concentrations observed in Keihin Industrial Center and their relation to meteorological elements 234

Review Articles:

G. NONHEBEL: The technical provisions of the British Clean Air Act—regulations for Scotland 241

Research in air pollution in the United Kingdom 242

Research in air pollution in Japan 249

Reports on Meetings:

G. NONHEBEL: 1958 Conference of the National Society for Clean Air 252

R. F. JONES: Atmospheric chemistry 255

Notes and News 256

Book Reviews:

"Air Pollution Control in New Jersey" (reviewed by PETER C. G. ISAAC) 258

"Appraisal of Air Pollution in Tennessee", by P. A. KENLINE (reviewed by PETER C. G. ISAAC) 258

"Berechnung der Ausbreitung von Staub und Gas", by M. DIEM and R. TRAPPENBERG (reviewed by W. KLUG) 259

"Sulphur Dioxide—Its Chemistry and Removal from Industrial Gases", by D. BIENSTOCK, L. W. BRUNN, E. M. MURPHY and H. E. BENSON (reviewed by H. E. NEWALL) 259

Papers accepted for publication 261

VO
1
1958

NUMBER 4

D. H. GREGORY and W. N. ADAMS: Smokeless fuels from high-volatile coals—I. The production of smokeless fuels by the mild devolatilization of a high-volatile coal *page* 263

A. F. GAINES and G. J. PITT: Smokeless fuels from high volatile coals—II. The smoke emission of low-temperature chars prepared from high-volatile coals 266

R. E. MUNN: The application of an air pollution climatology to town planning 276

T. A. RICH: The average size of submicron particles 288

Review Article :

L. W. POLLAK: Counting of Aitken nuclei and applications of the counting results 293

Notes and News 307

Book Reviews :

" Appraisal of Air Pollution in Texas " (reviewed by T. J. CHANDLER) 308

" Air Pollution Measurements of the National Air Sampling Network. Analysis of Suspended Particulate Samples Collected 1953–1957 " (reviewed by A. J. HAAGEN-SMIT) 308

Filmstrips (in colour) and Lecture Notes on Air Pollution (reviewed by J. F. DOWLER) 309

Papers accepted for publication 310

AUTHOR INDEX

ADAMS, W. N.	263	MEETHAM, A. R.	143
AMDUR, MARY O.	170	MIDDLETON, JOHN T.	155
BENTON, D. P.	44	MORTON, B. R.	184
BRUNELLE, MARGARET F.	51	MUNN, R. E.	276
CAREY, GEOFFREY C. R.	18	NONHEBEL, G.	120, 241, 252
COMMINS, B. T.	14	ODDIE, B. C.	114
DARLEY, ELLIS F.	155	ONO, Y.	234
ELTON, G. A. H.	44	PASQUILL, F.	60
FOX, F. T.	163	PEACE, E. A.	44
FUKUI, S.	234	PEAPLE, L. H. J.	103
GAINES, A. F.	266	PHAIR, JOHN J.	18
GALE, H. J.	103	PICKNETT, R. G.	44
GRAHAM, J. R.	110	PITT, G. J.	266
GREGORY, D. H.	263	POLLAK, L. W.	293
HAAGEN-SMIT, A. J.	51	RICH, T. A.	288
HANST, PHILIP L.	155	SCORER, R. S.	145, 198
IKEDA, H.	234	SHEPPARD, P. A.	31
JEHANNO, C.	221	SHEPHARD, ROY J.	18
JONES, R. F.	255	STEPHENS, EDGAR R.	155
KANNO, S.	231, 234	STEWART, N. G.	87
LALLEMANT, C.	221	STOCKS, PERCY	1
LUCAS, D. H.	71	STRAUSS, W.	139
MARSHALL, L. M.	163	THOMSON, MAURICE L.	18
MEADE, P. J.	60		

VOL.
1
958/9

VC
1
1958

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AIR POLLUTION AND CANCER MORTALITY IN LIVERPOOL HOSPITAL REGION AND NORTH WALES*

PERCY STOCKS
Colwyn Bay, N. Wales
(*Received* 23 *March* 1958)

Abstract—Filters designed to collect for analysis samples of the " smoke " present in the outdoor air at 17 localities in the Liverpool and North Wales region have been in operation continuously for periods of 1 to 3 years, and data are given of the average concentrations during 6 months in respect of total smoke, 3 : 4-benzpyrene, 1 : 12-benzperylene, pyrene, fluoranthene and sulphur dioxide. These are correlated with the density of population per acre and with the standardized mortality ratios for cancers of the lung and of the intestine.

Another 6 filters have operated in the Mersey road tunnel, a bus garage, a motor garage and an office in Liverpool, and comparisons are made between the concentrations of smoke and of its various constituents in the air inside and outside these confined spaces.

The work is continuing, with inclusion also of spectrographic analysis of trace elements, and only provisional conclusions can be drawn as yet.

INTRODUCTION

EVER since deaths have been registered in England and Wales the Registrar General's reports have been calling attention to the higher rates of mortality in the north and amongst town dwellers. In the period 1930–32 the standardized mortality ratios, that is the numbers of deaths registered per 100 of those calculated by applying age-specific death rates for the whole country to the group populations of each sex and age, were as follows amongst men and married women between the ages of 35 and 65 (REGISTRAR GENERAL, 1938).

TABLE 1

Social class	Men				Married women			
	County boroughs		Rural areas		County boroughs		Rural areas	
	North region	South† and east	North region	South and east	North region	South† and east	North region	South and east
I–II	113	93	86	76	100	85	94	80
III	115	93	84	71	112	92	107	80
IV–V	134	105	80	73	128	103	104	92

† Excluding Greater London.

Even in the rural districts there was within each social class a pronounced northern excess of mortality, and this was greater still in the large towns. The urban excess was greatest amongst men and larger in the north than the south.

* From data obtained for the British Empire Cancer Campaign in connexion with a Senior Fellowship held by the author, the research being then continued with a grant from the Medical Research Council.

VOL.
1
958/9

The excess of urban over rural mortality is particularly great for bronchitis and for cancer of the lung, as may be seen by comparing death rates at ages 45–64 in 1953 for the former and standardized mortality ratios in 1950–53 for the latter in large conurbations, small urban areas with less than 50,000 population and rural districts (REGISTRAR GENERAL, 1956).

TABLE 2

Class of area	Bronchitis, 1953 Rates per 100,000 at 45–64				Cancer of Lung, 1950–53 S.M.R. (all ages)	
	Males		Females		Males	Females
	North	South	North	South	All regions	All regions
Conurbations	158	131	37	29	126	121
Small urban areas	119	74	26	14	84	86
Rural districts	72	53	25	12	64	76

Statistical studies suggested that differences in occupations and in social conditions such as overcrowding within houses were partly responsible for the urban and northern excess for bronchitis, but this was not the case for lung cancer. Differences in mean air temperature between north and south contributed little to the geographical differences in death rates, but strong negative correlations were found between the total hours of sunshine recorded during 1930–32 in 20 towns and the standardized mortalities from bronchitis and lung cancer in those towns (STOCKS, 1947). No such relations with sunshine were found for other forms of cancer. If the average annual hours of sunshine recorded at places away from the large towns were compared for years 1930–32 according to geographical latitude, 24 of those south of 51° N gave 1576 hr and 26 places north of 53° N gave 1258 hr, and it was concluded that the deficiency in the latter arose mainly from cloud cover and smokiness of the air. It appeared that " either smokiness of atmosphere is an important factor in itself in producing cancer of the lung or sunshine is an important factor in preventing its incidence ".

The London fog of 1952, with its attendant high mortality from respiratory disease, produced at last a realization of the serious effects of air pollution upon health, and the paucity of knowledge about the chemical aspects of this problem became all too clear. Gaseous contaminants of air, grit and total suspended " smoke " had been studied, but little was known about the constituents of the smoke which was being inhaled or at least drawn into the nasal passages. The carcinogen 3:4-benzpyrene was detected in samples of atmospheric smoke by WALLER (1952), COOPER (1954) and KOTIN (1954), and this or associated hydrocarbons might well be concerned in the causation of respiratory cancer.

SOURCES OF DATA

In 1952 a field study of cancer incidence was started in North Wales and Liverpool Hospital Region as part of my plan of work with a British Empire Cancer Campaign Fellowship, integrated with proposals which had been made by the Cheshire and North Wales Group of the Campaign. The environmental factors to be studied included

the kind of atmosphere in which people lived and worked, and in 1954 the MEDICAL RESEARCH COUNCIL and the DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH decided to help this part of the survey by providing in the first instance 10 filters to operate continuously at suitable places in the region and laboratory facilities for analysing the smoke. The instruments, designed and provided by the FUEL RESEARCH STATION at East Greenwich, consisted of an electrically operated pump drawing air at a rate of about 10 m^3 per week through a short tube leading from outside the building to a Whatman No. 1 filter paper and gas meter within the building. The meter was read at a fixed time each week and the filter paper was changed at the same time or at longer intervals in places where the pollution level was low.

The filter papers were sent to the FUEL RESEARCH STATION for determination of total smoke by a photoelectric method and were then divided into two halves, one being sent to St. Bartholomew's Hospital for determination of the polycyclic hydrocarbons 3:4-benzpyrene, 1:12-benzperylene, pyrene and fluoranthene, the other being analysed spectrographically for the trace elements present in the smoke dust. Suitable numbers of filter papers were aggregated in order to obtain sufficient material for analysis, the resulting figures being usually 4 week averages for large towns and quarterly averages elsewhere.

The first series of 10 instruments operated from 13 October 1954 for 3 years. A preliminary report on the hydrocarbon concentrations, determined by CAMPBELL during the first 6 months was published in 1955 (STOCKS and CAMPBELL, 1955), and a report on the trace-element analyses carried out by K. V. AUBREY at the Fuel Research Station on the atmospheric dusts collected during 1955 was issued in 1956 (DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH, 1956). The filter sites had been chosen with a view to obtaining representative samples of air in places ranging from rural and small urban communities in North Wales and Cheshire to the densely populated conurbation of Merseyside. They were usually placed at offices of the Local Authority, avoiding proximity to sources of abnormal smoke emission, the air being taken at heights between 10 and 20 ft above ground level. The meter readings and change of filter papers were carried out for the most part by the Public Health Inspectors. At the same sites instruments were placed in the open air to measure the amount of sulphur dioxide by means of lead peroxide candles which were exposed for a calendar month and then changed, the analyses being made by the City Analyst at Liverpool.

In 1956 it was decided to install filters at 13 more places, 3 being in North Wales, 8 in Liverpool and 2 at other places in Lancashire. One was located on a hillside in Conway Valley in order to sample the purest air obtainable; two were placed in the Mersey road tunnel connecting Liverpool with Birkenhead, with another at the inlet of a ventilating shaft; two were fixed inside and outside a large bus garage, another inside a motor-car garage and another inside a large office in Liverpool. These filters began to operate in December, 1956, and were duplicated, a high-speed instrument working alongside the standard type to obtain larger quantities of dust for trace-element analysis.

The present report deals with the total smoke and its hydrocarbon content at the 23 stations during the 24 weeks from 24 October, 1956 to 10 April, 1957 and with sulphur dioxide during the 6 months October to March. The work at St. Bartholomew's Hospital since 1956 has been carried out by the M.R.C. Group for Research on Atmospheric Pollution, and B. T. COMMINS describes the technique and details the

VOL.
1
958/9

hydrocarbon figures in an accompanying paper (Polycyclic Hydrocarbons in Rural and Urban Air).

DESCRIPTION OF FILTER STATIONS

The sites chosen for air sampling which are dealt with in this report are of two kinds: (a) seventeen intended to estimate the average constituents of the outdoor air in which people live in the neighbourhood surrounding the instrument, and (b) six intended to measure the effects of motor traffic and exhaust fumes and to compare the air inside and outside buildings. These are detailed in Table 3, where series (a) are

FIG. 1. Location of air filters 1–17 in North Wales and Liverpool Hospital Region.

ranked in ascending order of the population of the village or town, nos. 1–10 having started to operate in October, 1954, and nos. 11–17 2 years later. Nos. 4, 7, 9, 10, 16–23 are in Merseyside conurbation, and the two maps show their positions. The purpose of nos. 18, 19 and 20 was to determine the amount of pollution added to air by the dense road traffic through the tunnel, and of nos. 21 and 22 to find how the hydrocarbon and trace-element concentrations can be affected by diesel and motor-

FIG. 2. Location of air filters in Liverpool and adjoining districts.

car exhaust fumes respectively within garages. The purpose of no. 23 was to find how air inside an office where many people are engaged in clerical work differs from that outside the office. The remaining localities are distributed over North Wales and Liverpool Hospital Region outside the conurbation as shown by the map of the whole region. No. 11 was out of reach of any chimney smoke other than that produced by the cottage where the filter was placed. Nos. 1, 2 and 12 were in aggregates of fewer than 1000 houses surrounded by open country. No. 13 was a slate-mining town surrounded by mountains, and no. 3 was located in an industrialized strip alongside the Dee estuary. Nos. 6 and 14 were in medium-sized towns with rural surroundings, nos. 8 and 15 in large industrial towns with rural areas to west and east.

TABLE 3(a). AIR FILTER STATIONS IN RELATION TO THE POPULATIONS SURROUNDING THEM

Serial number	Locality and county	Population		Site of filter	Kind of locality
		Census (thousands)	Persons per acre		
11	Conway Valley (Caernarvon)	6·2*	0·1	Caretaker's cottage	Hillside at 500 ft, near waterworks
1	Tattenhall (Cheshire)	1·1	0·6	Doctor's house	Village with factory, 7 miles S.E. of Chester
2	Llangefni (Anglesey)	2·2	0·9	Food inspector's office	Small market town in open country
12	Ruthin (Denbigh)	3·6	1·8	R.D. council office	Market town in open country
13	Blaenau Ffestiniog (Merioneth)	6·9	0·4	U.D. council office	Slate quarry town at head of valley
3	Flint (Flintshire)	14·3	2·1	P.H. inspector's office	Industrial town on west shore of Dee estuary
14	Ormskirk (Lancashire)	20·6	1·3	P.H. inspector's office	Market town with light industry in open country
4	Hoylake (Cheshire)	30·9	5·2	U.D. offices	Seaside residential area 10 miles W. of Liverpool
5	Wrexham (Denbigh)	31·0	10·6	County health office	Industrial town with coal mines to W. and S.
6	Chester (Cheshire)	48·2	11·6	Health office	Market and industrial town in open country
7	Bootle (Lancashire)	73·4	13·1	Health office	Northern part of Merseyside conurbation
15	Warrington (Lancashire)	80·7	18·3	Ambulance station	Large industrial town (engineering, etc.)
8	St. Helens (Lancashire)	110·3	13·9	P.H. inspector's office	Large industrial town (chemicals, glass, etc.)
9	Birkenhead (Cheshire)	142·4	16·6	Public health office	Port on Mersey estuary opposite Liverpool
10	Liverpool (Lancashire)	789·5	28·9	Princes Rd., N.H. office	1 mile S.E. of city centre
16	Liverpool (Lancashire)			Roe Street	¼ mile W. of city centre, and ¼ mile from river
17	Liverpool (Lancashire)			Edge Lane	Outside bus garage, 2 miles E. of city centre

* Population of Nant Conway R.D.

VOL. 1 958/9

TABLE 3(b). FILTER STATIONS FOR MEASUREMENT OF AIR POLLUTION IN ENCLOSED SITUATIONS

Serial number	Locality	Site of filter	Details of site
18	Liverpool	At Mersey Tunnel air intake shaft	Close to river, about 40 ft above ground level
19	Liverpool	In Mersey Tunnel, at mid-river point	Half way through tunnel, at its lowest point
20	Liverpool	In Mersey Tunnel, at road junction	At traffic lights where two outlets to Liverpool diverge
21	Liverpool	In a large bus garage in Edge Lane	Inside the garage (outside control see no. 17)
22	Liverpool	In a motor-car garage in Prescot Road	Inside the repair shop (same control as no. 21)
23	Liverpool	In National Health office, Princes Road	Large clerical room (outside control see no. 10)

AMOUNTS OF AIR POLLUTION IN TWENTY-THREE LOCALITIES

Table 4 shows the average concentrations of smoke (suspended matter arrested by the filter paper) in mg/100 m^3 of air passing through the filters, the amounts of four polycyclic hydrocarbons in p.p.m. of the suspended matter, and the concentrations of the same hydrocarbons expressed as μg/100 m^3 of air, during the 24 weeks from 24 October 1956, to 10 April 1957. At a few of the stations the date of starting was rather later, viz. 21 November at no. 4, 12 December at nos. 11, 12, 13 and 2 January at no. 14, the averages being based upon 20, 16 and 13 weeks instead of 24; but this could have had little effect on comparability since the average smoke index for 7 stations in the first 12 weeks of the period was 42·7 and in the second 12 weeks it was 41·8. In the last column are shown the daily average amounts of sulphur dioxide absorbed, expressed as mg of SO_3/100 cm^2 of lead peroxide (corrected to a standard batch), during the 6 months from 1 October to 31 March, 1956–57, or in the same months of 1955–56 at the places specified in the note below the table.

(a) *Representative locations*

The stations are arranged, as in Table 3, in ascending order of the population of the relevant area, which is also a rough measure of the number of chimneys. For Liverpool mean values of the results from the three stations will be used for correlation with population density and mortality.

Smoke concentrations ranged from 1·7 mg/100 m^3 of air in Conway Valley to 62·4 at Princes Road, Liverpool, following the population ranking rather closely. The only noteworthy variations from this were the rather low values at Hoylake which has the sea and Dee estuary to the west, at Chester where the filter was situated with a race course and river to the west, and at Birkenhead and Roe Street, Liverpool, which although in busy neighbourhoods were close to the Mersey estuary. The average at the first three stations in the table, which may be regarded as different types of " rural " location was 6·8, compared with an average of 53·1 in the large towns of Bootle, Warrington and St. Helens, and 57·5 in Liverpool. The mean for the 15 places, using the last-mentioned value for Liverpool, was 29·3 mg/100 m^3 with a standard deviation of 18·2.

TABLE 4. ATMOSPHERIC CONTENT OF SMOKE, POLYCYCLIC HYDROCARBONS AND SULPHUR DIOXIDE (WINTER AVERAGES) AT 23 LOCALITIES

Serial number	Location of air filter (see Table 3)	Smoke mg/100 m³	Hydrocarbons (p.p.m. of smoke)				Hydrocarbons (μg/100 m³ of air)				SO_3 per day*
			Benz-pyr-ene	Benz-pery-lene	Pyr-ene	Fluor-anth-ene	Benz-pyr-ene	Benz-pery-lene	Pyr-ene	Fluor-anth-ene	
(a) *Representative*											
11	Conway Valley	1·7	44	84	130	280	0·1	0·1	0·2	0·5	0·09
1	Tattenhall	10·8	24	77	76	110	0·3	0·8	0·8	1·2	0·49
2	Llangefni	7·2	51	74	42	59	0·4	0·5	0·3	0·4	0·30
12	Ruthin	13·9	33	140	60	59	0·5	2·0	0·8	0·8	—
13	Blaenau Ffestiniog	13·6	52	200	140	180	0·7	2·8	1·9	2·4	0·40
3	Flint	23·4	76	190	82	80	1·85	4·65	2·0	1·95	1·09
14	Ormskirk	29·8	74	230	67	110	2·2	6·9	2·0	3·3	2·50
4	Hoylake	16·9	20	160	61	86	0·3	2·7	1·0	1·5	1·37
5	Wrexham	34·3	57	145	52	56	1·95	5·1	1·85	1·95	0·83
6	Chester	27·8	57	160	68	70	1·45	4·0	1·7	1·8	2·01
7	Bootle	50·8	75	230	82	84	3·75	11·2	3·9	4·05	3·20
15	Warrington	57·3	80	160	62	83	4·4	8·6	3·45	4·6	2·49
8	St. Helens	51·3	89	210	90	115	4·75	10·9	4·7	6·05	3·64
9	Birkenhead	42·8	88	260	85	90	3·3	9·75	3·25	3·45	2·18
10	Liverpool — Princes Rd.	62·4	106	265	80	108	6·75	16·6	4·95	6·7	3·49
16	Liverpool — Roe Street	49·9	58	195	62	73	2·95	9·65	3·1	3·65	—
17	Liverpool — Edge Lane	60·3	74	195	78	84	4·5	11·6	4·8	5·1	3·08
(b) *Special sites*											
18	Tunnel, air inlet	41·0	52	135	34	41	2·15	5·5	1·4	1·7	5·31
19	Tunnel, midpoint	104·3	44	97	37	33	4·6	10·3	3·85	3·45	3·67
20	Tunnel, junction	202·7	21	101	31	28	4·2	20·8	6·35	5·7	4·32
21	Bus garage	60·5	103	160	65	45	6·2	9·8	4·0	2·8	0·86
22	Motor garage	70·0	76	195	119	99	5·3	13·7	8·15	6·9	—
23	Office interior	50·7	96	183	40	39	4·95	9·2	2·0	2·05	—

* No measurements taken at nos. 12, 16, 22, 23. Six-month average daily amount expressed as mg of SO_3/100 cm² of lead peroxide in October–March, 1956–57, except at nos. 2, 4, 6, 7, 8 where they relate to the 1955–56 period, the instruments being moved to other stations in 1956.

The hydrocarbon content can be considered in two ways, either of which might be important if any harmful effects result from contact with the respiratory epithelium. If the smoke contains an unusually large amount of a carcinogenic hydrocarbon it might be more injurious on that account even though the total amount of the substance being inspired in a unit of time is not excessive. Alternatively if the chemical composition of the smoke was the same in all localities the amount of a hydrocarbon being inspired would increase with the total smoke concentration and its injurious effects might increase accordingly. In Table 4, therefore, measures are given both per million parts of smoke and per 100 m³ of air. It should be noted that the " blackness " of smoke, on which the photoelectric measurement of the total smoke depends, varies to some extent, diesel smoke being " blacker " per unit weight than ordinary mixed smoke. Since the smoke concentration has to be used to calculate the hydrocarbon values in air, the latter are also affected by this and are of course subject also

VOL. 1 958/9

to their own errors of measurement. The figures in the table are arithmetic means of the analytical figures obtained in successive equal periods of time, the final digits being of little import for the reasons given above. At station no. 11 a very small quantity of smoke was available for analysis even from 16 weeks of continuous air filtration and the hydrocarbon figures are subject to larger errors than elsewhere.

Benzpyrene content per million parts of smoke averaged 40 in the rural localities compared with 79 in Liverpool and values of 80 or more in Warrington, Birkenhead and St. Helens. For benzperylene the rural average was 78 compared with 218 in Liverpool and higher values still in Ormskirk, Bootle and Birkenhead. Pyrene and fluoranthene showed no consistent change in this measure of the concentration in relation to urbanization. It appears that the smoke in large towns is richer in benzpyrene and benzperylene than is the smoke in rural and small-town situations, but that this is not the case for pyrene and fluoranthene. The correlations with population density are examined in the next section.

Sulphur dioxide indices averaged about 0·3 at the rural stations, increasing to about 2 at Chester and Birkenhead, 2·5 at Ormskirk and Warrington and over 3 in Liverpool, Bootle and St. Helens, the ratio to total smoke being fairly constant.

(b) *Special sites in Liverpool*

(i) *Mersey tunnel.* The road tunnel with four traffic lanes from Liverpool to Birkenhead is entered at each end by two approaches converging into the main tunnel which is about $1\frac{3}{4}$ miles long. There are 6 ventilating stations providing up to $2\frac{1}{2} \times 10^6$ ft^3 of air per hr, and a filter (no. 18) was placed at an air inlet on the roof of the main control station. The lower concentration of the smoke here as compared with the heart of Liverpool as sampled at stations 10, 16 and 17 may be due to proximity to the river or to height above ground level. Another filter (no. 19) was placed at the mid-point of the tunnel where the lowest level is reached, and a third (no. 20) at the road junction where the Liverpool approach tunnels meet and are controlled by traffic lights with much consequent waiting of motor vehicles at this point.

TABLE 5

Site of filter	Smoke dust	Hydrocarbons in smoke				Hydrocarbons in air				SO_2 index
		Benz-pyrene	Benz-perylene	Pyrene	Fluor-anthene	Benz-pyrene	Benz-perylene	Pyrene	Fluor-anthene	
(A) Air inlet	100	100	100	100	100	100	100	100	100	100
Mid-point	254	85	72	109	80	214	187	275	203	69
Junction	494	40	75	91	68	195	378	454	335	81
(B) Street air	100	100	100	100	100	100	100	100	100	100
Mid-point	181	56	44	51	38	97	82	90	67	112
Junction	352	27	46	42	32	89	165	148	111	132

Two comparisons can be made for the air in the tunnel at stations 19 and 20, namely (A) in terms of corresponding measures of the air entering the ventilating shaft at station 18 taken as 100, and (B) in terms of the average street air in Liverpool at stations 10, 16, 17 taken as 100. The results are shown in the Table 5 above.

Smoke concentration in the air was 2½ times as great at the mid-point and about 5 times as great at the junction as in the air entering the inlet of the ventilating shaft at St. George's Dock. The " smoke " in the tunnel contained smaller amounts of benzpyrene, benzperylene and fluoranthene than that in the entering air and about the same amount of pyrene. At the mid-point the smoke was about half as rich in each of the hydrocarbons as was the smoke in Liverpool streets; and at the road junction it was half as rich in benzperylene and pyrene and about one third as rich in the other hydrocarbons as the street air.

These results could arise by addition to the entering air (with its content of town smoke) of " smoke " produced by traffic which is not so rich in the hydrocarbons. The net effect on the amounts of air at the mid-point of the tunnel was to raise the concentrations of benzpyrene, benzperylene and fluoranthene to about double and that of pyrene to 2¾ times the levels in the entering air; and at the junction the ratios were from 2 to 4½. In comparison with the general town air there was no excess at the middle of the tunnel for any of the hydrocarbons, but at the road junction the ratio for benzperylene was about 1⅝ and for pyrene 1½.

(ii) *Bus garage*. Two sets of instruments were fixed at a large bus garage in Edge Lane, one filter taking air from inside the garage (no. 21) and the other taking air from outside, away from the entrance (no. 17). Comparison between these in Table 4 shows that the smoke concentration was the same inside and out. The concentrations of hydrocarbons were of similar order inside and outside the garage but the analyses were not accurate enough to establish whether any differences between them were significant.

VOL. 1 958/9

(iii) *Motor-car garage*. An air filter was placed inside the repair shop of a motor garage in the same neighbourhood as the bus garage and comparison can be made again with no. 17. Smoke showed excess of 16 per cent and again the concentrations of hydrocarbons were of similar order inside and outside.

(iv) *Office interior*. Comparison between the air inside (no. 23) and outside (no. 10) the large office room at Princes Road shows that the smoke concentration inside was rather lower than it was outside the window, and the smoke inside was not so heavily charged with any of the hydrocarbons. This suggests that during working hours clerks in a large room are exposed to rather lower concentrations of the hydrocarbons than are workers outside in the same neighbourhood of a city.

TABLE 6

Filter site	Smoke in air	Hydrocarbons in smoke				Hydrocarbons in air			
		Benz-pyrene	Benz-perylene	Pyrene	Fluor-anthene	Benz-pyrene	Benz-perylene	Pyrene	Fluor-anthene
Bus garage	0	X	0	0	—	X	0	0	—
Motor garage	0	0	0	XX	0	X	0	XX	X
Mid-tunnel	XX	—	—	—	—	0	0	0	—
Tunnel junction	XX	—	—	—	—	0	XX	X	0
Office interior	0	—	—	—	—	—	—	—	—

The indications in respect of air pollution in enclosed spaces are summarized above, making comparison with no. 17 for the garages, nos. 10, 16, 17 for the tunnel and

no. 10 for the office, ratios below $\frac{3}{4}$ being denoted by —, between 0 and $1\frac{1}{4}$ by 0, between $1\frac{1}{4}$ and $1\frac{1}{2}$ by X, and over $1\frac{1}{2}$ by XX.

TABLE 7. STANDARDIZED MORTALITY RATIOS FOR CANCER OF THE LUNG AND BRONCHUS AND OF THE INTESTINE AND RECTUM IN THE ADMINISTRATIVE AREAS SURROUNDING FILTERS OF SERIES (a)

Serial number of filter	Administrative area	Cancer S.M.R.		Serial number of filter	Administrative area	Cancer S.M.R.	
		Lung and bronchus	Intestine and rectum			Lung and bronchus	Intestine and rectum
11	Nant Conway R.D.	59	129	5	Wrexham M.B.	78	132
1	Tarvin R.D.	70	55	6	Chester C.B.	112	107
2	Llangefni U.D.	53	92	7	Bootle C.B.	146	106
12	Ruthin M.B.	15	77	15	Warrington C.B.	115	114
13	Ffestiniog U.D.	62	126	8	St. Helens C.B.	111	94
3	Flint M.B.	74	154	9	Birkenhead C.B.	132	108
14	Ormskirk U.D.	95	83	10, 16, 17	Liverpool C.B.	158	109
4	Hoylake U.D.	98	115				

CORRELATION BETWEEN AIR POLLUTION AND CANCER OF THE LUNG AND INTESTINE

Table 7 shows the standardized mortality ratios (s.m.r.) for cancer of the lung and bronchus (international nos. 162, 163) and for cancers of the intestine and rectum (nos. 152–154) in administrative areas around the air filters of series (a) in Tables 3 and 4. For lung cancer the deaths of residents in the period 1950–54 are expressed in terms of the numbers expected taken as 100. The expected deaths were calculated by multiplying the deaths in those years in England and Wales at ages 0–, 35–, 45–, 55–, 65–, 75 and over for each sex by the corresponding ratios of the local to national census population and aggregating the 12 products. For intestinal cancer an eight-year period was used. The ranking of the areas is the same as in Table 3 which shows the population densities per acre and Table 4 which gives the air-pollution indices. It is evident that the s.m.r.'s for lung cancer correspond closely with the amount of population around the filter site, whereas intestinal cancer shows no such obvious relation.

Table 8 gives the correlation coefficients between the various pollution indices and population density, lung cancer mortality and intestinal cancer mortality. Since population density is highly correlated with smoke concentration, correlation between the latter and the cancer indices could arise if population density affects cancer incidence for some reason independent of smoke. Consequently, in the case of lung cancer partial second order coefficients have been calculated to measure the correlation between lung cancer incidence and air pollution when the population per acre is held constant, the coefficients in the fourth column showing the correlations with lung cancer which would result if the 15 areas all had the same density of persons per acre. This eliminates any contribution which the density factor may make by itself to the first order coefficients. In the same way the coefficients in the fifth column show the residual correlations with population density and sulphur dioxide concentration when total smoke is held constant.

Taking an example, lung cancer incidence and smoke are highly correlated to the extent of 0·826, but each is highly correlated with population density, the coefficients being 0·830 and 0·889 respectively. The partial coefficient between lung cancer and smoke when density of population is constant is given by the formula:

$$\frac{0{\cdot}8265 - (0{\cdot}8305 \times 0{\cdot}8890)}{\sqrt{1-(0{\cdot}8305)^2}\,\sqrt{1-(0{\cdot}8890)^2}} = 0{\cdot}346.$$

TABLE 8. CORRELATION COEFFICIENTS BETWEEN MORTALITY FROM CANCERS OF LUNG AND INTESTINE IN 15 AREAS AND POPULATION DENSITY, SMOKE, HYDROCARBON AND SULPHUR DIOXIDE CONTENT OF AIR*

	Coefficients (first order) with			Coefficients (second order)	
	Population per acre	Cancer of		Population per acre constant	Smoke constant
		Intestine	Lung	Lung	Lung
Population per acre	—	−0·006	0·830	—	0·371
Smoke per unit volume of air	0·889	−0·040	0·826	0·346	
3:4-benzpyrene, p.p.m.	0·617	0·097	0·633	0·276	
1:12-benzperylene, p.p.m.	0·516	0·138	0·654	0·477	
Pyrene, p.p.m.	−0·194	0·219	−0·055	0·194	
Fluoranthene, p.p.m.	−0·338	0·107	−0·212†	0·133	
3:4-benzpyrene/m³ of air	0·850		0·792	0·293	
1:12-benzperylene/m³ of air	0·844		0·851	0·496	
Pyrene/m³ of air	0·813		0·823	0·447	
Fluoranthene/m³ of air	0·764		0·764	0·361	
Sulphur dioxide absorbed from air	0·428	−0·234	0·493	0·273	0·150

* For sulphur dioxide 14 areas only (see note to Table 4). For all the measurements relating to Liverpool the mean figures at localities 10, 16 and 17 have been used since cancer mortalities are known only for the whole city.

† If Conway Valley (where the fluoranthene figure is doubtful) is excluded the correlation coefficient is −0·043.

The number of unit areas being 15, coefficients below 0·48 are not statistically significant at the conventional 1 in 20 level, and a correlation of 0·35 might arise by chance about once in five trials. Lung cancer is highly correlated with smoke concentration and when population per acre is held constant a moderate correlation remains. Similarly lung cancer is highly correlated with population density (0·830) and when smoke concentration is held constant this falls to 0·371. From this it appears that, whilst smoke is an important contributor to the excess of lung cancer found in large towns, other factors are also contributing to this, such as the rather higher rate of heavy cigarette smoking in towns. By way of contrast, intestinal cancer gives no correlation either with smoke or with population density, and there is no need to calculate partial coefficients.

Benzpyrene content of the smoke is correlated to the extent of 0·63 with lung cancer, and when population density is constant a coefficient of 0·28 remains, but with intes-

VOL. 1 958/9

tinal cancer there is no correlation. Concentration of this hydrocarbon in the air is more highly correlated with lung cancer (0·79) and the partial coefficient is 0·29. The partial coefficients might have arisen by chance once in 3 or 4 trials with 15 stations.

Benzperylene content of the smoke is correlated similarly with lung cancer (0·65), and the partial coefficient of 0·48 is significant at the conventional 1 in 20 level, but with intestinal cancer there is no appreciable relation. Concentration per unit volume of air is more highly correlated with lung cancer (0·85) and when population density is held constant a coefficient of 0·50 remains which is significant at the conventional level.

Pyrene and fluoranthene per unit weight of smoke show no appreciable relations with either lung or intestinal cancer, but their concentrations per unit volume of air correlate with lung cancer to the extent of 0·82 and 0·76; and when population density is constant the partial coefficients are 0·45 and 0·36 respectively, neither figure being quite significant at 0·05 level.

Sulphur dioxide indices correlate to the extent of 0·49 with lung cancer mortality, reduced to 0·27 when density of population is held constant and to 0·15 when total smoke is constant, the independent relation with lung cancer being small and of doubtful significance.

There is definite evidence that an association exists between lung cancer mortality and population density. The concentration of smoke in the air appears to be one of the factors contributing to this, but so far in this investigation insufficient data have been collected to establish with certainty the magnitude of the contribution made by smoke*.

Of the hydrocarbons, 1:12-benzperylene, whether measured per unit weight of smoke or per unit volume of air, is correlated significantly with lung cancer mortality independently of the density of population in the district; 3:4-benzpyrene shows correlations of the same kind but not quite significant at the conventional level. From present evidence the correlations with the other hydrocarbons are not suggestive of independent association with lung cancer. Neither smoke nor any of the hydrocarbons show any appreciable association with intestinal cancer.

FURTHER RESEARCH

Continuation of this method of investigation with a larger number of filter stations has been made possible by a grant from the Medical Research Council. New instruments have been installed at 5 more places in Lancashire and 6 in Yorkshire in December, 1957, and 3 have been added in Tyneside in March, 1958. Trace-element analysis of the smoke at most of the stations is also being done at the Fuel Research Station and it will be possible to correlate the results with cancer mortality. Furthermore a statistical study has been started of cancer and respiratory disease mortality in relation to population distribution and wind direction throughout a wide region in the north of England and Wales, and this will provide an independent method of measuring the connexion between domestic chimney smoke and incidence of these diseases.

* In 48 districts of a larger area extending to the West Riding of Yorkshire, for which data of smoke concentration are available, a statistically significant partial correlation of 0·256 remains with lung cancer when population density is held constant, and further work is in progress on this.

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VOL.
1
958/9

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POLYCYCLIC HYDROCARBONS IN RURAL AND URBAN AIR

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(*Received* 18 *April* 1958)

Abstract—This report deals with the determination of polycyclic hydrocarbons in the smoke collected during the winter of 1956–57 from rural and urban atmospheres in Great Britain. The analyses were done as part of the British Empire Cancer Campaign's Cancer Survey (STOCKS, 1958). The smoke samples were collected on filter papers in urban and rural districts of North Wales, Cheshire and Lancashire, and the weight of smoke on the filters assessed by reflectance measurements. The smoke papers were extracted in acetone; the extract was reduced carefully to dryness and redissolved in *cyclo*hexane. The hydrocarbons in this extract were then chromatographically separated on a column of activated alumina and the amounts of each hydrocarbon determined in bulked eluates by ultraviolet spectrophotometry. The amounts of pyrene, fluoranthene, 3:4-benzpyrene and 1:12-benzperylene were determined at each of the 23 sites sampled and the results expressed as parts of hydrocarbon per 100,000 parts of smoke and μg of hydrocarbon/m^3 air. The results showed that the concentration of hydrocarbons was much lower in rural than in urban areas. The errors in measurement of the hydrocarbons are discussed.

INTRODUCTION

THIS report is concerned with the measurement of polycyclic hydrocarbons in urban and rural atmospheres as part of the British Empire Cancer Campaign's Cancer Survey (STOCKS, 1958). Small quantities of polycyclic hydrocarbons have been found in samples of atmospheric smoke collected in both urban and rural parts of North Wales, Cheshire and Lancashire. The amounts of pyrene, fluoranthene, 3:4-benzpyrene and 1:12-benzperylene were generally sufficient for quantitative analysis; anthracene was also found in amounts too small for accurate determination.

COLLECTION OF SMOKE SAMPLES

The smoke samples were collected by drawing air at 500 ft^3/week through Whatman No. 1 papers held in 4 in. diameter brass filter holders. A gas meter in series with the pump recorded the amount of air drawn through the filter. The weight of smoke on the paper was assessed by measuring the density of the stain with a reflectometer. The filter papers were changed weekly in large towns and less frequently in other areas; this ensured that each filter collected a measurable amount of smoke without becoming blocked.

ANALYSIS OF SMOKE

Papers from each site were pooled to give samples for periods of 12 weeks. The outer unstained edges were discarded and the papers were cut into several pieces, placed in a soxhlet apparatus and extracted for 3 hr with 200 ml of acetone. The extract was then slowly reduced to a bulk of about 30 ml before being brought to dryness by gentle evaporation at room temperature with hand bellows. The residue was then dissolved with gentle warming in a few ml of redistilled *cyclo*hexane, the

solution transferred to a small beaker and reduced to a volume of about 1 ml by evaporation of the solvent at room temperature, again with the hand bellows. From this *cyclo*hexane solution the polycyclic hydrocarbons were separated chromatographically using a short alumina column. The alumina (3 g of Peter Spence activated 100/200 mesh) was kept over 50 per cent v/v sulphuric acid for at least 24 hr, after which it was mixed to a slurry with *cyclo*hexane and poured into a glass chromatographic column 15 × 1 cm; a plug of *cyclo*hexane-washed glass wool was used to support the alumina. The column was developed initially with 35 ml of *cyclo*hexane which eluted all the pyrene and fluoranthene. The 3:4-benzpyrene and 1:12-benz-

TABLE 1. CONCENTRATION OF SMOKE AND HYDROCARBONS OF RURAL AND URBAN AREAS (24 OCTOBER 1956–10 APRIL 1957)

Location of smoke samples*	Average smoke concentration (mg/m³)	Amount of hydrocarbons in the smoke (parts per 100,000)				Concentration of hydrocarbons in the air (μg/100 m³)			
		Pyrene	Fluoranthene	3:4-benzpyrene	1:12-benzperylene	Pyrene	Fluoranthene	3:4-benzpyrene	1:12-benzperylene
Conway Valley† (Caernarvon)	0·02	13	28	4	8	0·2	0·5	0·1	0·1
Tattenhall	0·11	8	11	2	8	0·8	1·2	0·3	0·8
Llangefni	0·07	4	6	5	7	0·3	0·4	0·4	0·5
Ruthin†	0·14	6	6	3	14	0·8	0·8	0·5	2·0
Blaenau Ffestiniog†	0·14	14	18	5	20	1·9	2·4	0·7	2·8
Flint	0·23	8	8	8	19	2·0	2·0	1·8	4·6
Ormskirk‡	0·30	7	11	7	23	2·0	3·3	2·2	6·9
Hoylake§	0·17	6	9	2	16	1·0	1·5	0·3	2·7
Wrexham	0·34	5	6	6	14	1·8	2·0	2·0	5·1
Chester	0·28	7	7	6	16	1·7	1·8	1·4	4·0
Bootle	0·51	8	8	8	23	3·9	4·0	3·8	11·2
Warrington	0·57	6	8	8	16	3·4	4·6	4·4	8·6
St. Helens	0·51	9	12	9	21	4·7	6·0	4·8	11·0
Birkenhead	0·43	9	9	9	26	3·2	3·4	3·3	9·8
Liverpool									
Princes Road	0·62	8	11	11	26	5·0	6·7	6·8	16·6
Edge Lane (outside bus garage)	0·61	8	8	7	20	4·8	5·1	4·5	11·6
Bus Garage (inside)	0·60	6	4	10	16	4·0	2·8	6·2	9·8
Mersey Tunnel									
Air inlet	0·41	3	4	5	14	1·4	1·7	2·2	5·5
Liverpool Junction	2·02	3	3	2	10	6·4	5·7	4·2	20·8
Mid-River Point	1·04	4	3	4	10	3·8	3·4	4·6	10·3
Motor Garage	0·70	12	10	8	20	8·2	6·9	5·3	13·8
Office Interior (Princes Rd.)	0·51	4	4	10	18	2·0	2·0	4·9	9·2
Roe Street	0·50	6	7	6	20	3·1	3·6	3·0	9·6

* For further details see STOCKS (1958) (Air Pollution and Cancer Mortality in Liverpool Hospital Region and North Wales).

† 12 December 1956–10 April 1957. ‡ 2 January 1957–10 April 1957.

§ 21 November 1956–10 April 1957.

VOL. 1 958/9

perylene were then eluted with 5%, 10% and finally 20% solutions of benzene in *cyclo*hexane. All the 1:12-benzperylene was eluted when 60 ml of solvent had passed through the column. The actual volume of solvent needed to elute the hydrocarbons depends largely on the amount of smoke analysed and the figures given above represent typical amounts. The eluates were conveniently collected in tubes of about 3 ml capacity and the ultra-violet absorption of each fraction measured at the wavelengths given by COOPER (1954). The pyrene and fluoranthene tubes were pooled and the solution evaporated to small bulk by means of the hand bellows. Similarly pooled fractions containing benzpyrene and later fractions containing benzperylene were separately evaporated to dryness with the bellows and redissolved in *cyclo*hexane. These three fractions were then made up to standard volumes (2·7, 5 or 10 ml, depending on the amount of material present) and the weight of the hydrocarbons determined in 10 mm or 2 mm cells with the Unicam SP.500 spectrophotometer using the standard optical height given by COOPER (1954). The results were expressed as μg of hydrocarbon/g of smoke and per 100 m^3 of air.

The concentrations of smoke and polycyclic hydrocarbons are given in Table 1. The average smoke concentration varied from 0·02 to 2·0 mg/m^3; benzpyrene concentrations were between 0·1 and 6·8 μg/100 m^3 and those of pyrene between 0·2 and 8·2 μg/100 m^3.

DISCUSSION

Pyrene can be determined without much difficulty as it exhibits a strong absorption peak at 335 mμ. Fluoranthene also has a strong absorption peak at 287·5 mμ but towards the end of its elution from the chromatographic column 1: 2-benzanthracene (with an absorption peak at 288·5 mμ) begins to appear. The measured amount of fluoranthene may include some 1:2-benzanthracene as these two absorption peaks are very close together.

The determination of 3:4-benzpyrene can also be subject to error as its measurement depends upon the use of a weak absorption peak at 403 mμ. This peak can be masked by the absorption from other materials present; considerable errors may arise if only small amounts of benzpyrene are present. To reduce the error large samples of smoke were used for analysis where possible. The determination of 1:12-benzperylene depends to some extent upon the amount of benzpyrene measured and in cases where errors arise in the determination of benzpyrene further error will arise in the benzperylene measurement. The errors of measurement of 3:4-benzpyrene described above occur only in a few cases particularly when analyses of less than 10 mg of smoke are being undertaken. When dealing with such small samples no satisfactory alternative analytical procedure can be applied but for larger samples where masking of the small benzpyrene peak is apparent a more complete chromatographic separation of 3:4-benzpyrene and 1:12-benzpyrene can be carried out, spectral analysis of each 3 ml eluate made and the benzpyrene determined by measuring the larger peak at 385 mμ, using the smaller 403 mμ peak only to indicate the presence of the hydrocarbon. In the few fractions where benzperylene (which has also a peak at 385 mμ though not at 403 mμ) is also present the actual optical height of the 403 mμ peak is used to estimate the benzpyrene. The excess of the ratio of the small to the larger 385 mμ peak compared with the ratio in a solution containing pure benzpyrene is used to calculate the amount of 1:12-benzperylene present in these mixed fractions.

All solvents used in the analysis were distilled twice and all glassware cleaned thoroughly in chromic–sulphuric acid mixture. The Fuel Research Station, Greenwich was responsible for siting the sampling stations, collection of papers and assessment of smoke concentrations.

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VOL.
1
958/9

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SOME FACTORS IN THE DESIGN, ORGANIZATION AND IMPLEMENTATION OF AN AIR HYGIENE SURVEY*

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Abstract—In 1952, a project was initiated in Cincinnati which had as its primary objective the solution of problems encountered in the design, organization, and implementation of morbidity surveys attempting to relate human reactions to the low levels of atmospheric contamination commonly found in urban areas of the United States. A preliminary report has already appeared (PHAIR and THOMSON, 1956). Three pilot surveys have now been completed. The time thus seems appropriate to review the experience gained from nearly 2000 patient-visits, and to make certain recommendations with regard to both planning and operation of future, larger scale, air hygiene surveys.

THE THREE SURVEYS

THE main features are summarized in Table 1. Each was organized in the city of Cincinnati and continued for a period of approximately 3 months. Selected groups of cardio-respiratory cripples confined to their homes were closely followed by nursing and medical staff, subjective and objective assessments of physiological state being obtained simultaneously with detailed measurements of domestic and external environment.

TIMING OF SURVEYS

The general level of pollution rises progressively with the onset of winter, when meteorological conditions favor the accumulation of contaminants, and steady industrial sources are supplemented by the domestic heating load (CHOLAK *et al.*, 1952; PHAIR *et al.*, 1958). Seasonal fluctuations of air pollution are of some importance in the timing of surveys, since animal experimentation and studies in industrial plants have demonstrated considerable adaptation to adverse physical and chemical environments (PATTLE and CULLUMBINE, 1956; LEHMANN, 1893; KEHOE *et al.*, 1932; ANDERSON, 1950; AMDUR *et al.*, 1953).

Two distinct types of short-term prospective air pollution surveys may be envisaged. In one, exemplified by the second and third pilot surveys, observations commence in the early autumn, when subjects may be relatively unaccustomed to contaminated atmospheres; in the second, exemplified by the first pilot survey, observations commence later in the winter when most subjects may have some degree of adaptation.

CHOICE OF SUBJECTS

The study of human reactions to air pollution may have either of two mutually exclusive aims. One is to study the behavior of a selected, rigidly defined, group of

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patients in a given experimental situation; the second is to characterize the parent population from which a sample is drawn at random. In each pilot survey the first procedure was adopted. Two main reasons governed this decision: (1) practical considerations limited the number of subjects to a figure that could not be considered representative of a parent population; (2) it was thought desirable to concentrate attention on susceptible individuals. A selected group of patients may quite reasonably form the population for a prospective survey, although in a larger scale effort it might be preferable to relate the sample to a more general parent population.

TABLE 1

Problem	Pilot survey one	Pilot survey two	Pilot survey three
Timing	January–April 1955	September–December 1955	October–December 1956
City	Cincinnati	Cincinnati	Cincinatti
Subjects	15 Male 13 Female (14 cardiac, 8 chest, 6 mixed lesions)	18 Male 16 Female (17 cardiac, 12 chest, 5 mixed lesions)	6 Male 4 Female (5 cardiac, 5 chest)
Selection criteria	Shortness of breath Residence in smoky area Confinement to home Ability to keep diary	As in one	As in one
Residence	Home 26 Institution 2	Home 19 Institution 15	Home 2 Institution 8
Visits	Half thrice weekly Half twice weekly	Half thrice weekly Half twice weekly	All thrice weekly
Staff			
Medical	One	Two	Two
Registered nurses	Three	One	One
Practical nurses	—	Three	Two
Technicians	One	One	Three
Statistical clerk	Two	Two	One
Computer operator			One
Electronic computer	IBM 704* (General Electric)	IBM 704* (General Electric)	Burroughs E, 102 (Departmental)

* Electronic computations not yet started.

The criteria adopted in selecting the patients are summarized in Table 1. The clinical and physiological status of each patient was assessed by clinical and radiographic examination, together with a wide range of pulmonary function tests. Cardiorespiratory cripples were selected since there is good evidence from both London (BEAVER, 1954) and Donora (ASHE, 1952) that the increase in mortality during episodes of acute pollution occurs mainly in patients with pre-existing cardiac or respiratory disease. In the case of cardiac patients, it is not necessarily true that physiological

VOL.
1
958/9

changes produced by a contaminated atmosphere are more severe than in normal individuals; death may be merely a consequence of the greatly reduced initial cardio-respiratory reserve. However, there is evidence that patients with respiratory abnormalities, particularly a tendency to bronchospasm, show an increased response to irritants such as SO_2 (VAN SIM, personal communication). The effective concentration of an irritant gas is also greatly affected by the degree of ciliary activity and mucus formation in the bronchi (DALHAMN, 1956). Ciliary activity is depressed in most forms of chronic respiratory disease, but, on the other hand, bronchial mucus formation may be increased. In the last pilot surveys, patients were specifically questioned with regard to the weather and their general condition. Three of the ten (two with bronchitic asthma and emphysema, one with extensive pulmonary fibrosis of unknown etiology) admitted sensitivity to " fog ", while four of the " respiratory " patients were also adversely affected by damp weather.

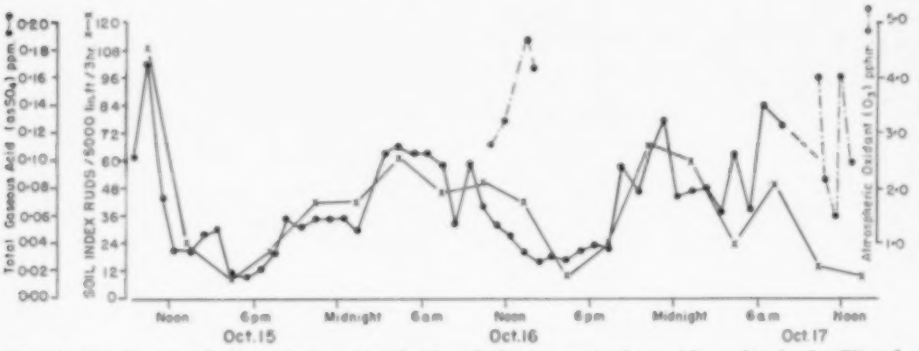

FIG. 1. The pattern of atmospheric contamination during an acute thermal inversion in the City of Cincinnati.

Certain disadvantages must be set against the possible greater sensitivity of respiratory cripples: (1) The patients may not be able to co-operate as well as healthy subjects in the performance of physiological tests. In fact, the co-operation of the old people (whose ages ranged from 54 to 83 years) was remarkably good, as is emphasized by the coefficients of variation for the tests used (SHEPHARD *et al.*, 1958a, b). (2) Days may be " lost " through acute exacerbations of the patient's illness. This disadvantage is largely outweighed by days " lost " through outings in a patient who is not sufficiently confined to his house. In the last survey, only eight visits were sacrificed out of a total of 340, six being attributable to illness, and two to trips out of town. (3) Day-to-day variations in the patient's condition may be attributable to changes in the disease state rather than in the level of atmospheric contamination. In the allergic form of asthma, sensitivity to house dust, ragweed pollen, and other time-related variables may be particularly confusing, and this type of patient was therefore rigidly excluded from the surveys.

The patients formed a rather selected group from the standpoint of social status, quite a high proportion living in old peoples' homes and institutions. This class presents several convenient features from the viewpoint of survey organization: (1) Diversions are few, and many of the old people are glad of an occasional visit from the nurse or doctor. (2) Furnishings are not elaborate, and sampling apparatus is readily

introduced. (3) Even relatively fit patients rarely leave the institution. (4) Where two patients share the same room, it is possible to economize on sampling equipment. It was thought originally that one set of environmental measurements might be adequate for an entire institution, but two and even threefold gradients of both particulate matter and gaseous acid were found between rooms, depending on whether windows and doors were kept open or closed (Fig. 2).

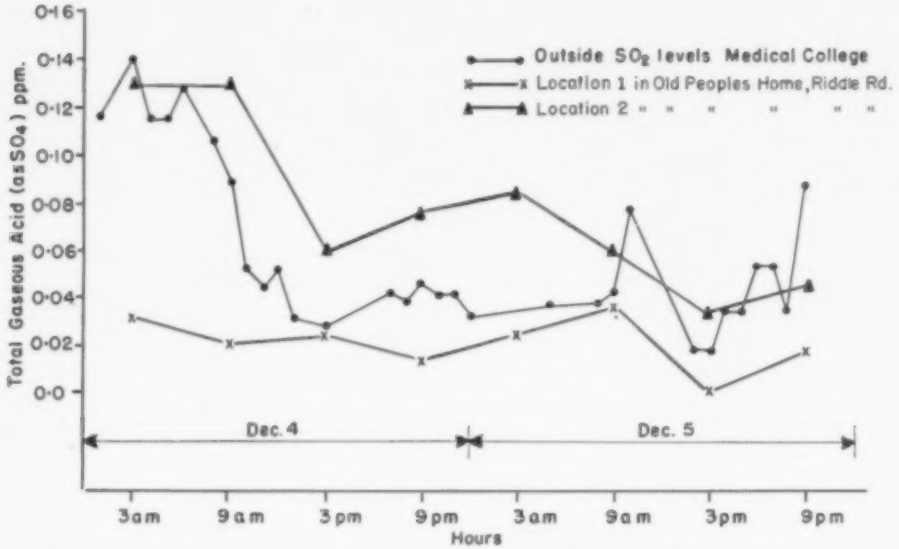

FIG. 2. Comparison of internal and external gaseous acid levels in different parts of a large institution.

A possible criticism of institutional patients is the opportunity for collusion in the preparation of diaries. This hazard was minimized by using a small number of patients from four independent institutions.

FREQUENCY OF VISITS

Patients do not tolerate more than an average of three visits per week over a long period, and to avoid additional visits by technicians it is necessary to train the nurses to service sampling equipment. During the first two surveys, the nurses visited 5 days a week, seeing some patients on Mondays, Wednesdays, and Fridays, and the remainder on Tuesdays and Thursdays. This left the data unbalanced, complicating subsequent statistical analysis. In the third survey, patients were visited 3 days a week, Tuesdays and Thursdays being devoted to analysis of records. The timing of visits was also controlled to within $\frac{1}{2}$ hr or less. This was more convenient for the patients, and statistical analysis was simplified by the exact time base. Another important feature was a laboratory technician on 24 hr call in case of mechanical failure of the environmental sampling apparatus. This considerably reduced the number of " lost " observations (a serious problem in previous surveys).

During the first two surveys, the nurses had little supervision after the initial period of training, and important differences of technique developed as the surveys progressed. To control this tendency in the third survey, one of the medical staff checked the

VOL. 1 958/9

technique of each nurse and each patient regularly once a fortnight. These periodic visits also enabled a closer watch to be kept on the general clinical condition and environment of the patients.

DAILY ROUTINE DURING SURVEY

Between 7 a.m. and 8 a.m. one of the medical staff and two technicians prepared and checked the apparatus required for the day's work, the largest tasks being the filling of ten portable gas cylinders, the evacuation of some thirty gas sampling bottles, and the filling of as many as a hundred sulphur dioxide sampling vials.

The nurses arrived at 8 a.m. and collected fresh supplies of diary forms and other procedure sheets, while the technicians loaded into their cars a pulmonary pressure gauge, a timed vital capacity apparatus, a portable box-bag and ancillary equipment, racks of sulphur dioxide sampling vials, supplies for the thermohygrographs and Hemeon samplers, and a psychrometer.

During the morning, each nurse visited three patients by car, spending approximately 1 hr with each patient. Her duties included the checking of diary entries, the taking of pulse, temperature and respiration, the carrying out of lung function tests, and the servicing of sampling apparatus. The thermohygrograph was checked against the psychrometer, and adjustment made if the error was greater than three points. Few of the thermohygrographs needed re-setting more than once during the survey. The timing of the Hemeon smoke sampler was checked to ensure that there had been no failure of the power supply since the last visit, and on a fixed day each week a new roll of filter paper was inserted. With the gaseous acid sampler, the nurse recorded which tube was bubbling on arrival, and when the solenoid valve closed she inserted the new rack of tubes.

At noon, the nurses returned to the laboratory and the samples of CO–helium mixture were analyzed at once so that the same equipment could be used again for the afternoon visits. The SO_2 samples were analyzed during the afternoon while the nurses visited the remainder of the patients. With only ten patients and three external sampling stations, the work of analysis was still quite heavy, some 100 separate gas analyses and 150–250 conductivity measurements being carried out each day.

SUBJECTIVE AND NURSING OBSERVATIONS

Two industrial field surveys, which were carried out recently by the Kettering Laboratory, have shown that the use of standardized questionnaires by qualified medical personnel can yield information that is as valuable as most field tests of lung function in diagnosing the presence of respiratory disease. However, when questions are asked repeatedly and forms are completed by patients and practical nurses, the method may be less reliable. This problem has been investigated and is reported elsewhere (SHEPHARD *et al.*, 1958d). Briefly, only four main types of forms were used in the air pollution studies. Two of these were completed by the nurse on her first visit and gave details of (1) other persons living in the same household and (2) the type of housing, furnishings, and methods of heating and ventilation. Another form was completed by the nurse at each visit and provided information regarding changes in medical treatment, residence, or smoking habits of the patient. The fourth type of form was the multiple entry diary (Fig. 3) which was filled in daily by the patient and was examined by the nurse at each visit.

AIR POLLUTION SURVEY 1956

PATIENT DIARY

Date ..... Day ..... Patient's No. .....

		12–6 a.m.	6–12 a.m.	12–6 p.m.	6–12 p.m.
Cough	Less than usual				
	Usual amount				
	More than usual				
Short of breath	Less than usual				
	Usual amount				
	More than usual				
Sputum	Less than usual				
	Usual amount				
	More than usual				
Wheezing	Less than usual				
	Usual amount				
	More than usual				
Chest pain	.....				
Running nose	.....				
Sore throat	.....				
Headache	.....				

Away from home:

Where? ..... When? ..... How long? .....

House-Cleaning

Date: ..... Time: .....

Cooking involving frying or oven-roasting

Date: ..... Time: .....

Medicines

Remarks

FIG. 3. Multiple-entry diary sheet used by patients in third survey.

Analysis of these forms has shown the following results: (1) 3 per cent of all diary sheets are lost or spoiled by patients. (2) About 40 per cent of patients show a progressive decrease in the variance of their recorded symptoms, suggesting that less and

VOL. 1 958/9

less consideration is being given to accurate reporting of their subjective reactions. (3) More meticulous patients record their symptoms accurately for the entire 3 month period of survey, and there seems no doubt that a group of patients selected objectively by means of monthly analyses of variance would provide useful information from their diaries for even longer periods. (4) The majority of patients show an increase of symptoms after periods of increased air pollution. (5) The periodic opening of windows and the presence of tobacco smoke affect the accuracy of measurements of suspended particulate matter in the home (SHEPHARD *et al.*, 1958c). (6) Little information is contributed by the nurses' own descriptions of symptoms, breathing pattern, and illness in other members of the household, largely because of their limited medical training.

CHOICE OF PHYSIOLOGICAL TESTS

At least four criteria govern the choice of objective, physiological tests of pulmonary function. These are: (1) simplicity; (2) reproducibility of results; (3) sensitivity in detecting changes produced by atmospheric contaminants; and (4) a clear relationship to abnormalities of pulmonary physiology. The present surveys have shown that, provided both nurses and patients are trained with patience and care, fairly complex tests can be carried out in a meaningful way on domestic premises. However, in order that a nurse may see a reasonable number of patients in a day, it is essential to keep tests as simple as is commensurate with reasonable accuracy. The reproducibility of the test procedures has been discussed elsewhere (SHEPHARD *et al.*, 1958a, b). Briefly, the box-bag measurements of carbon monoxide uptake are as good as can be obtained by laboratory procedures; the variability of the pulmonary dynamic measurements is rather greater than reported for normal laboratory subjects, but it is doubtful if any great improvement could be obtained under field-survey conditions. A more critical question is whether the " correct " aspects of respiratory function are being tested. The original hope was to discover one test that would serve as an objective index of impairment of human health. Recent factor analyses of respiratory function tests (GILSON and HUGH-JONES, 1955; SHEPHARD *et al.*, 1958) suggest that at least three or four " pure " tests would be necessary to build up even a partial picture of pulmonary function, but if the relative importance of different " pure " factors could be determined, it might still be possible to devise one test incorporating elements of the factors that are most affected by atmospheric contaminants.

The aim of the three pilot surveys was to use relatively " pure " tests. The pulmonary pressure measurements measured mainly the power of the thoracic musculature, the untimed vital capacity measured static capacity and the timed vital capacity, mainly the airway resistance, particularly when expressed as a percentage of the untimed capacity. In the second survey, some attempt was made to evaluate the relative importance of bronchospasm and increased bronchial secretions in altering airway resistance by noting the effect of " aerolone " inhalations on the timed vital capacity; however, this was found to be too time consuming to recommend it for extensive field use. A simple aneroid gauge (Fig. 4) and plastic mouthpiece was adequate for the recording of pulmonary pressure, although the nurses' task could have been simplified by the addition of a ratchet mechanism to indicate the maximum pressures developed. In the first survey, a water-filled spirometer was used for the vital capacity measurements, but this proved unduly cumbersome; a McKesson–Scott bellows instrument fitted with Gaensler time-

VOL.
1
1958/9

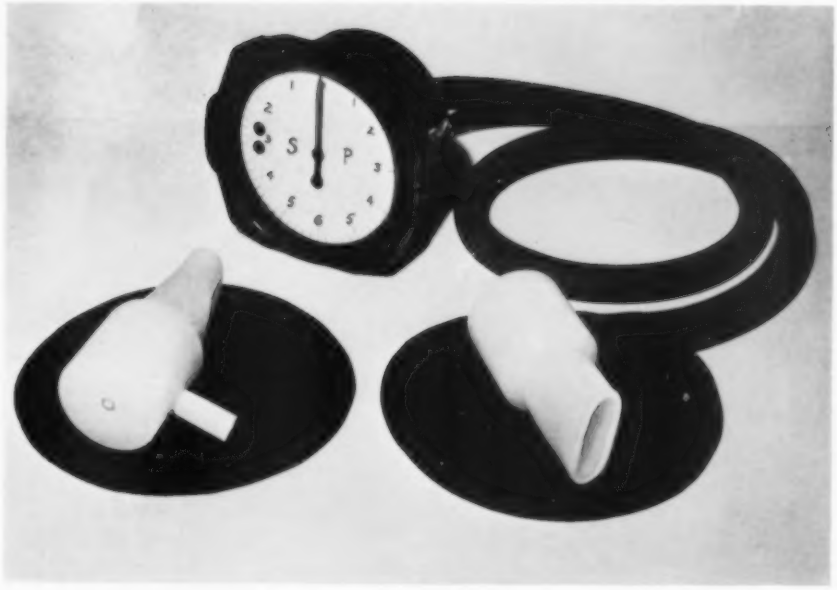

FIG. 4. Pulmonary pressure gauge and mouthpiece.

FIG. 5. Portable bellows-spirometer.

VOL.
1
958/9

FIG. 6. Wood–Geraci oximeter and carrying case.

FIG. 7. Portable box-bag as used in third pilot survey.

switch and indicating pulley proved a very efficient substitute (Fig. 5) with mechanical properties superior to the water-filled apparatus.

In the earliest survey, an attempt was made to test gas transfer aspects of pulmonary function using a Wood–Geraci type oximeter (Fig. 6). The possibility of using this instrument in the field has recently been raised once again (PECORA, 1957). Quite extensive experience with this instrument convinced us it was unsuitable for air hygiene studies of the type under present consideration. The galvanometer is too delicate for repeated transport to and from the homes of patients, and even if it is accepted that an arterial puncture can be omitted, the initial adjustment of the apparatus places a severe strain on the capabilities of the average nurse. Further, to obtain significant results it is necessary to perform a quite severe standardized exercise test, and we have felt unwilling to permit this in severely disabled patients without medical supervision. A more promising approach to field measurements of gas transfer is currently being developed in this laboratory; the original version of what we are terming " the portable box-bag " (CAREY *et al.*, 1957) was available for inclusion in the 1956 survey, and gave useful values for both functional residual capacity and carbon monoxide uptake (Fig. 7). More recent developments now permit the calculation of absolute values for the diffusing capacity, ventilatory efficiency and effective pulmonary blood flow. Apparatus of this type is more portable and simpler to use than the oximeter; further, direct comparison of the two methods in over 80 subjects has shown that the box-bag gives a much more sensitive index of impaired pulmonary diffusion, even if the oximeter measurements are made during exercise.

VOL.
1
958/9

Two important aspects of respiratory function—airway resistance, and lung compliance—were not measured directly. Airway resistance is known to change during exposure to gaseous irritants (AMDUR and MEAD, 1955; VAN SIM, personal communication), although the effect has not been demonstrated in man at naturally occurring concentrations. In the three surveys, airway resistance was assessed by timed vital capacity measurements. These are simple and very reproducible, but are affected by a number of factors in addition to airway resistance. The interrupter technique (OTIS and PROCTOR, 1951) gives a more direct value for airway resistance, and work is now proceeding in this laboratory to adapt this method to field survey work. There is good reason to believe that pulmonary compliance is also modified by exposure to

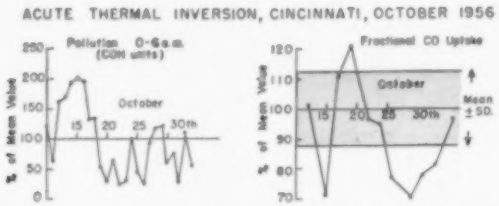

FIG. 8. Changes of pulmonary function during and immediately following acute thermal inversion. Mean values for ten cardio-respiratory cripples.

atmospheric irritants (AMDUR and MEAD, 1955) but to measure this quantity it is necessary either to enclose the subject in a respirator or to get the subject to swallow an esophageal tube. Some subjects can become relatively accustomed to the latter procedure, and the idea of finding subjects who would be prepared to swallow a

balloon on say thirty occasions cannot be dismissed as impracticable. However, the positioning of the tube in the esophagus is very critical (MEAD and WHITTENBERGER, 1953). Compliance measurements would thus seem best reserved for a small-scale specialized project under close medical supervision.

The relative sensitivity of the different field tests in detecting changes produced by air pollutants is presently being assessed by a multiple regression technique. However, preliminary analysis of data for the week following an acute inversion episode (SHEPHARD *et al.*, 1958e) has shown a very significant decrease of carbon monoxide uptake some five days after the first smoke peak, with little change in the measurements of pulmonary dynamics (Fig. 8).

ENVIRONMENTAL MEASUREMENTS

Quite wide variations in environmental conditions have been demonstrated between different areas of Cincinnati, and where transient peaks of pollution have been recorded, these have varied by as much as 24 hr in timing. This may be related in part to the complicated topography of a city that was originally built on seven hills and has since spread to several others, but important variations between different sampling stations seem likely even in cities built on relatively flat sites. Where reliance is placed upon externally situated sampling units, a further very important source of error is the existence of significant gradients between the inside and outside of domestic premises. Changes in concentration of gaseous acid within a room where windows and doors are closed lags 1½–2 hr behind changes in the external environment, and, perhaps even more significant, the sharp peaks of concentration that are such a typical feature of the outdoor record on a gusty day are not observed (PHAIR *et al.*, 1958). Two basic criteria of experimental design are consequent upon these findings: (1) Subjects must each be confined to one small section of the total city environment. (2) Continuous and accurate measurements must be made of changes in the composition of this micro-environment.

TABLE 2. GASEOUS ACID AND SUSPENDED PARTICULATE MATTER IN CINCINNATI

Average values from third pilot survey, October–December, 1956. (Three external sampling stations, downtown values usually 50 per cent above average for three stations.)

Reading	Gaseous acid (p.p.m.)	Particulate matter (COH units/1000 linear ft)
Maximum 1 hr value*	0·143	14·5
Maximum 24 hr mean value	0·12	5·44
Minimum 24 hr mean value	0·017	0·56
Average for 3 months	0·042	1·89

* Downtown location.

The ideal subject would be completely confined to his home, but in practice such subjects are usually not fit enough to co-operate in repeated evaluations of pulmonary function. The old person who is fit enough to make a journey perhaps once a week to church or to the neighborhood store seems a suitable compromise; it is possible to record in detail the timing of such excursions, and usually such journeys are made at times when the level of contamination is low (midday). One set of recording appar-

atus is probably adequate to indicate the average micro-environment of a suburban house, although to minimize error the sampling units were in the bedroom, since in Cincinnati (contrary to the experience in Britain) peak levels of pollutants are observed mainly at night. It has already been emphasized that in larger buildings such as the old peoples' institutions, several recording units are necessary.

In the first two studies, continuous micro-environmental records of temperature and humidity and hourly measurements of suspended particulate matter were obtained. In the last study, 6 hr sequence sampling of gaseous acid was added to this routine. There have been suggestions that there is a correlation between cardio-vascular and respiratory deaths and changes of temperature and humidity, and since these variables were easily measured, it was thought a sound principle to eliminate variance due to them before attempting to measure changes related to air pollution. The value of the A.I.S.I. apparatus in providing an index of suspended particulate matter requires little comment, although it may be emphasized that mean particle size and color differ appreciably indoors, particularly in the presence of tobacco smoke (SHEPHARD *et al.*, 1958c). The regression analysis is also proving the value of sequence sampling of gaseous acid. In some parts of the city, there is only a limited correlation between gaseous acid and suspended particulate matter (Fig. 9).

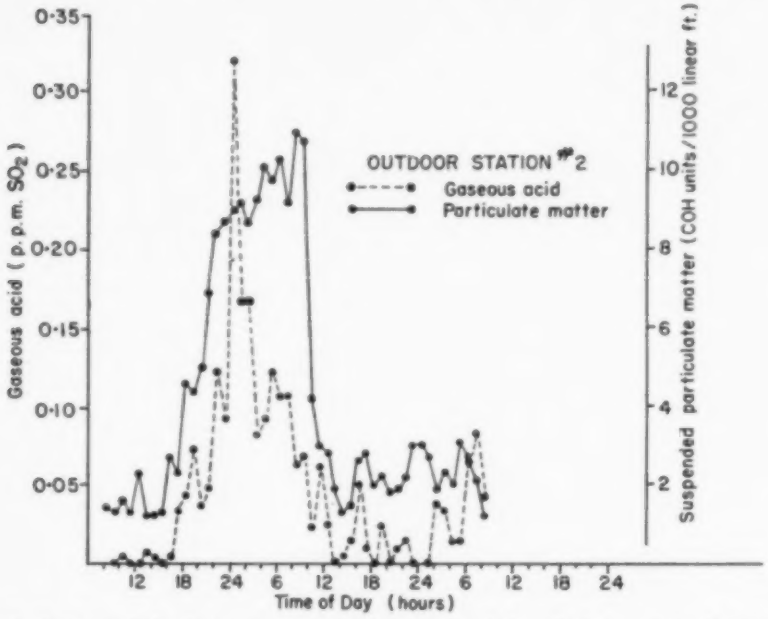

FIG. 9. Lack of correlation between gaseous acid and suspended particulate matter. External sampling station in industrial area.

The value of external sampling stations requires some explanation. External humidity measurements are important in connection with the oxidation of sulphur dioxide. Hourly external samplers for gaseous acid help to establish details of the relationship between gaseous acid and suspended particulate matter, although this relationship is by no means constant from one part of a town to another, or indeed in the same

location at different seasons (Phair *et al.*, 1958). It cannot be over-emphasized that the number of external stations required to give an overall picture of pollution in a hilly city such as Cincinnati is so large as to forbid serious consideration.

All equipment was enclosed in special cabinets which were relatively soundproof and reasonably attractive as items of furniture (Fig. 10). These were locked to prevent interference by inquisitive children (or adults!). Small but powerful fans mounted in the rear walls insured an equality of environment inside and outside the cabinet. No more than occasional complaints were received, and these originated from members of the household other than the patients.

CHOICE OF PERSONNEL FOR SURVEY

It remains to discuss the number and type of personnel required for a field survey project of this nature. The patient visits demand above all a sympathetic person with a genuine understanding of people—someone who is prepared to share in items of gossip, and maintain a gentle discipline regarding the keeping of diaries and participation in the special tests. A moderate amount of intelligence is necessary to handle the pulmonary function tests, but details of the manipulations can be learned in a week of intensive training. We have found practical nurses well suited to this work. Visits to individual patients took about 1 hr, and most of this time was usefully spent. It is well recognized that where reliance is placed mainly upon a questionnaire, 50 per cent or more of the nurse's time is occupied with the pleasantries of a visit. However less time is lost if a smaller number of patients is tested in more detail. Allowing for time taken in driving, the nurses were able to see five patients quite comfortably in the course of an 8 hr day, while on the days that they were not making visits adequate time was available for analysis of thermohygrograph and smoke deposit records. The immediate supervision of the practical nurses was entrusted to a fully qualified industrial nurse. Her other responsibilities consisted of electronic gas analysis, the checking of data sheets, and the calculation of values such as the carbon monoxide uptake—work that might have been carried out more easily by a trained laboratory technician. A good medically trained laboratory technician would probably be able to handle information collected by three or even four practical nurses.

A technical assistant is required to measure the conductivity of solutions from the sequence samplers. Three or four 1 hr stations and ten 6 hr stations provide quite a full day's work for one person. A further assistant is required to service the external stations; with practice, one man could service six or seven machines in different parts of a town.

Finally, an adequate " shop " for the repair of faulty machines is essential. The work of the shop can be materially reduced, but not eliminated, if all machines are carefully checked before the survey is initiated. The repair shop requires the most experienced assistant of all, as the minor causes of breakdown in sampling apparatus can only be learned over a long period.

We have not been able to convince ourselves that a project of this type can operate efficiently unless every aspect of the work is closely supervised by trained research personnel, preferably with a medical background. The ratio of patients to trained research personnel could no doubt be increased as a project developed, but with the present range of tests it is doubtful if worthwhile information could be collected where this figure exceeded twenty to one.

VO
1
1958

VOL.
1
958/9

FIG. 10. Domestic environmental sampling apparatus in sound-proof cabinet.

VO
1
1958

The statistical handling of the data requires one clerk and one computer operator per ten patients. The value of a statistician of consultant status is unquestionable, but there is much to commend the more direct supervision of computations by a person with some grounding in laboratory work, for instance a physiologist with some knowledge of statistics, since normal values for the derived figures will be better understood by such a person, and mistakes that are costly in terms of electronic computer time may for this reason be avoided. Similar very practical considerations govern the choice of electronic computer; our first two studies were designed for analysis by the very complex IBM 704 machine, and two years were spent in obtaining a suitable operating program. The third survey was designed for the much simpler Burroughs E.102 machine. This does not handle the data so rapidly, but the program can be written by the average physiologist statistician in an hour, and an ordinary statistical clerk can be taught to operate the machine in an afternoon.

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THE EFFECT OF POLLUTION ON RADIATION IN THE ATMOSPHERE

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(*Received* 24 *March* 1958)

Abstract—Absorption and scattering by a polluted atmosphere are considered in relation to:
(a) Solar radiation (wavelengths 0·3–3 μ)
(b) Terrestrial radiation (wavelengths 3–60 μ).

Scattering and absorption by particulates are considered in the light of Mie theory, in regard both to the polar diagram of scattered light and to the extinction cross-section as a function of wavelength, particle diameter and refractive index. Single scattering is mainly forward but multiple scattering, which is significant for transmissions less than about 0·75—transmission of solar radiation by a heavily polluted column may often be less than this limit—results in a greater fraction of backward scatter.

Some observations of WALDRAM on polar diagrams of scatter and on transmission over the bottom kilometre of a polluted atmosphere are quoted to show that more than 30 per cent of the solar beam may be scattered and more than 25 per cent absorbed by the column. Of the 30 per cent or more scattered probably less than half would be lost to the atmosphere by upward scatter.

Observations of solar radiation, direct and diffuse, in central London and on its periphery, provide further values of scatter and absorption which point in the same direction as do those of WALDRAM.

Terrestrial radiation appears to suffer significant absorption by particulates even in a rural atmosphere and it is much stronger in London. The effect is to increase the cooling rate of the bottom kilometre or so of the polluted atmosphere by as much perhaps as 2° or 3°C per day. The ground surface must then cool somewhat less by terrestrial radiation. Computations by MÖLLER on a model atmosphere containing a given distribution and amount of particulate matter are broadly in line with this conclusion.

Thus there is significant upward scatter of solar radiation by pollution—a loss of heat to the atmosphere—and a significant absorption, which replaces a corresponding absorption at the ground. The absorption of solar radiation is offset by increased emission of terrestrial radiation by the layer concerned, and the latter loss will be dominant in mid-winter conditions when solar energy is necessarily small.

VOL.
1
958/9

1. SCOPE

THERE are, effectively, two distinct beams of radiation passing through the atmosphere; solar radiation in which the energy is almost completely confined within the wavelength limits of 0·3 μ and 3 μ ($1\mu = 10^{-4}$ cm), and terrestrial radiation originating in the atmosphere and at the earth's surface in which the energy is practically confined within the limits 3 μ and 60 μ (Fig. 1). It is physically convenient to discuss the effects of pollution on radiation in each band separately because the particles constituting pollution react somewhat differently to the two beams—for the solar beam the wavelength λ is comparable with the particle diameter d whereas for the terrestrial beam λ is mostly materially greater than d—and because the terrestrial beam is excited by the radiating material, including pollution, in the atmosphere. The remainder of the paper will be used to elaborate this theme, with particular reference to the energy balance of the atmosphere.

I shall necessarily use the word pollution to refer to all particulate matter, other than cloud, present in the atmosphere. Much of this particulate is not, of course,

man-made, but its effect on radiation is essentially the same whatever its source. There will be differences in degree according to location with respect to sources of pollution, natural or man-made.

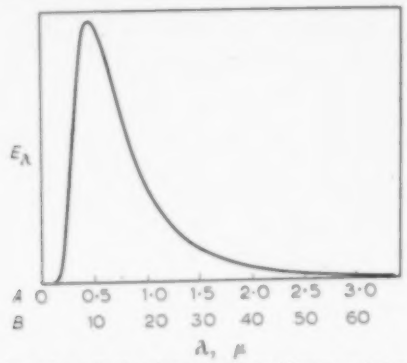

FIG. 1. Distribution of black-body radiation intensity E (arbitrary units) against wavelength λ (μ) for:
(A) Black body at 6000°K (approximation to sun)
(B) Black body at 300°K (earth's surface at given temperature).

2. EFFECT OF ATMOSPHERE ON SOLAR RADIATION

2.1 *Gaseous atmosphere—no particulate present*

It is appropriate to note first, briefly, the effect of the pure gaseous atmosphere on the downwardly directed solar beam. There are two processes by which the beam is affected:

(a) Absorption, i.e. direct conversion of radiant energy into thermal energy.
(b) Scattering, i.e. re-direction of radiant energy without change in total.

Absorption is effected mainly as shown in Table 1:

TABLE 1

Gas	Spectral region	Region of absorption	Percentage fraction of incident beam absorbed
Ozone	Ultra-violet	Stratosphere	5–8
Water-vapour	Infra-red	Troposphere	5–8
		Total	10–17

The significance of the absorption by water-vapour may be judged by the fact that it would, on its own, cause a warming of the troposphere of about 0·5°C per day, independent of height.

It has been suggested (Frenkiel) but by no means demonstrated that ozone is produced in significant amount near the earth's surface as a product of pollution. It is unlikely that such ozone, if present, would significantly affect the absorption figures given above since most of the available solar energy has been absorbed already by stratospheric ozone.

Sulphur dioxide and carbon monoxide and dioxide, as atmospheric pollutants, do not give rise to significant additional absorption in the solar spectrum.

The scattering of solar radiation by the molecules of the air is of the well-known Rayleigh form ($d/\lambda \ll 1$) given by

$$I_s \propto \frac{I_0}{\lambda 4}(1+\cos^2\theta)$$

where I_0 is the incident intensity and I_s the intensity of light scattered at an angle θ to the incident beam. The polar diagram of scattered light—the diagram produced by the end-point of the I_s vector as it is rotated through 360° in any plane containing the incident beam—is an ellipse slightly squeezed at the minor axis so that equal amounts of energy are scattered forward and backward, and $I_{s,90°} = \frac{1}{2}I_{s,0°} = \frac{1}{2}I_{s,180°}$. The bulk result is that 10 to 30 per cent of solar radiation incident on the atmosphere is scattered from the direct beam—the lower the solar elevation the more the scatter—and rather more than half of this is scattered back to space because there is multiple scattering.

Gaseous absorption and scattering together are then seen to account for a loss from the direct beam at ground level of about 20 to 50 per cent, depending on time of day in the main. The loss in downward-directed radiation is however less, some 15 to 35 per cent, because of the downward scattered radiation from the sky. These figures provide a kind of foot-rule against which to judge the importance of additional losses from the solar beam by pollution.

VOL.
1
958/9

2.2 *Atmosphere with particulates*

We now come on to very difficult ground, in that the absorption and scattering of radiation by *specified* particulates, with dimensions comparable with the wavelengths of the radiation, are highly complex phenomena and we do not even in general know all the relevant properties of the particulates comprising atmospheric pollution. For these reasons it is natural to attempt to infer the effects of pollution on solar radiation by direct measurement of the solar beam and of the light scattered from it in atmospheres with varying degrees of pollution. There is a very large and disorderly literature on the subject, which is what generally happens when observation is not guided by some semblance of theory. I shall not be able to unravel the skein in this paper but will attempt a short statement of principle and some interpretation of observations. A much more comprehensive but still succinct statement of principle is given by GREEN and LANE (1957), and a full treatment is given by VAN DE HULST (1957).

The absorption and scattering by a cloud of particulate matter depends on:

(a) The ratio of the particle diameter d to the wavelength λ, usually expressed in terms of the ratio $\alpha \equiv \pi d/\lambda$.
(b) The refractive index m of the particle relative to the medium, this parameter being generalized to $n - in'$ when the particle material has an absorption coefficient $k_a \propto n'(i \equiv \sqrt{-1})$, and a real refractive index n ($= m$ for $n' = 0$).
(c) The optical depth of the medium along the line of propagation.

There is a comprehensive rigorous theory due to Love, Mie and Debye for the intensity of radiation I_s scattered in a given direction θ with respect to the incident beam I_0 by a spherical particle, giving $I_s/I_0 = f(\alpha, m, \theta)$. Unfortunately the function f is expressed

in terms of a slowly convergent series so that a tremendous labour of computation is involved to cover the required ranges of the variables on which f depends. Substantial computations have been published by LOWAN (1949) and GUMPRECHT and SLIEPCEVICH (1954) and a bibliography to the literature is given by KERKER (1955) and VAN DE HULST (1957).

The polar diagram of scatter for a particle is an oval on which in general are many small and some large corrugations—the former of no significance in the present context. For a water droplet ($n = 1{\cdot}33$) the ratio of direct forward to backward scatter increases very rapidly with α, from unity for $\alpha \leq 0{\cdot}3$ ($d \leq 0{\cdot}2\mu$ for $\lambda = 1\mu$) to 10^3 for $\alpha = 3$ and to 10^4 for $\alpha = 30$ which is about the largest value of present interest. For opaque particles however (very high n) the asymmetry is in the opposite sense. Pollution particles do not consist of water but they are in general hygroscopic and it has been found (ADEN and KERKER, 1951) that even with a very thin coating a particle scatters as if composed of the coating material. A haze top in the atmosphere, viewed obliquely downwards, does in general look much brighter into the sun than with the sun behind one and WALDRAM (1945), to whose work we shall refer below, found nearly always that the forward scatter from a small volume of air was one or two orders of magnitude greater than the back scatter in industrial haze. With such rapid possible variation of the I_s vector with θ, it may be that the fractions of solar energy scattered downward and upward (as opposed to forward and backward) may vary considerably with solar elevation, effects of multiple scattering apart (see Section 2.3)

If one is concerned solely with the loss of radiation from the direct beam, this is given by integrating the scatter over all angles and adding the absorption by the

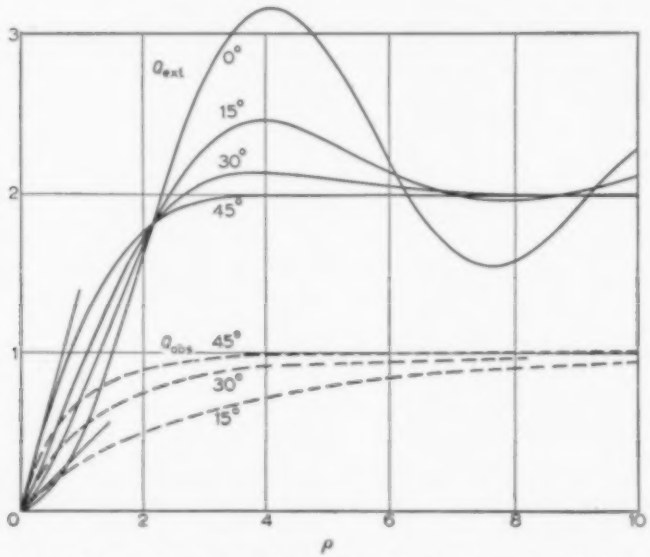

FIG. 2. Extinction and absorption cross-sections (full and broken lines respectively) as a function of $\rho = 2\alpha(n-1) = 2\pi d(n-1)/\lambda$ and of $\beta = \tan^{-1}(n'/(n-1))$. The refractive index is $n - in'$ where n is the real part (as commonly listed) and n' is proportional to the absorption coefficient k_a. For $|n - in'|$ of order unity. (Reprinted with permission from: H. C. VAN DE HULST (1957) *Light Scattering by Small Particles*, p. 181. Wiley, New York.)

particle. The former is commonly expressed as the relative *scatter cross-section* K_s of the particle and is the total fraction of the incident energy which is scattered from the direct beam. The absorption may be similarly expressed as the relative *absorption cross-section* K_a and the sum of K_s and K_a is termed the relative *extinction cross-section* K_e. The absorption cross-section (the qualification " relative " will now be dropped) is of course of direct interest to our study but is rarely available in published tables. The scatter cross-section, which is much better documented, is of less interest, since the loss to the earth of solar radiation by scatter is the energy scattered upward which is proportional to some (varying?) fraction of K_s. The general behaviour of K_e, K_s, and of K_a as far as it is known, for refractive index $|m|$ of order unity is shown for spheres in Fig. 2. The curve for $\beta=0$ (no absorption) is the case $K_e=K_s$ and it shows the oscillatory nature of the scatter function with variation of α or λ. To the left of the maximum, scatter increases with decrease of λ (blue scattered more than red), and to its right, up to the minimum, the opposite variation occurs. Beyond the limit of the diagram, K_s fluctuates with diminishing amplitude to an asymptotic value of 2. (The asymptotic value is 2 because, at large distances, the geometrical shadow of the particle is filled by light diffracted round the edges of the particle. The inclusion of this diffracted light in the scattered light doubles the scatter cross-section.) Only with the rarely occurring mono-disperse aerosols (once in a blue moon!) will the effects of alternating slope of the K_s, ρ curve be apparent in the atmosphere. The curve for $\beta=0$ is given by $K_s=2-(4/\rho)\sin\rho+(4/\rho^2)(1-\cos\rho)$ and is valid for water droplets (and most hygroscopic particles?) in the visible spectrum. When the particulate is absorbing, as for water in the solar infra-red, or for carbon and tarry particulates throughout the spectrum, the other curves of Fig. 2 are relevant, with $K_s=K_e-K_a$. Thus, for a carbon sphere (chains are perhaps as common in the atmosphere) $n=1{\cdot}59-0{\cdot}66i$ giving $\beta=50°$ which is, appropriately for the pollution study, about the limit of the diagram. We see from the figure that there is considerable scatter from such particles for low values of ρ or α, but that there is effectively no scatter other than diffracted light in the " shadow " for $\rho>3$ ($\alpha>2{\cdot}5$, $d>0{\cdot}4\mu$ for $\lambda=0{\cdot}5\mu$).

VOL.
1
958/9

2.3 *Bulk action of particulates*

The total effect on scatter and absorption by a cloud of particles is obtained by a simple summation over all the particles in the path provided the path length and density of the aerosol are not so large that secondary or multiple scattering is significant. If multiple scattering occurs the evaluation of the integral effect becomes exceedingly difficult. As a rough rule it is safe to assume single scattering if the transmission of the direct beam is not reduced to less than $e^{-0{\cdot}1}$ ($=0{\cdot}90$) by passage through the aerosol, there is some effect of secondary scattering if the transmission is between $e^{-0{\cdot}1}$ and $e^{-0{\cdot}3}$ ($=0{\cdot}74$), and for transmissions of less than $e^{-0{\cdot}3}$ multiple scattering prevails. The inevitable effect of multiple scattering is to increase absorption, if the particulate is absorbent, and otherwise to increase the fraction of energy scattered backward. (It is for this reason that a natural cloud appears bright in reflected light, though the individual droplets of the cloud scatter much more strongly forward than backward.) Not the least difficulty in the pollution problem is that extinction in heavy pollution does commonly exceed that for which single scatter treatment is appropriate. The latter treatment will however provide lower limits of absorption and back scatter.

No attempt is made here to exploit the theory of single scattering in a quantitative evaluation of the extinction of solar radiation by atmospheric pollution. The theory has however lately reached the stage at which such an evaluation, in terms of known or reasonably inferred properties of pollution aerosol, could be tackled with some hope of success. It is also possible of course to obtain information on the properties of pollution aerosol by experiment and use of the single scatter theory. Recent work is considered by VAN DE HULST (1957, Chap. 20). Dispersion of particle size may make interpretation difficult.

2.4 *Observations on extinction properties of polluted atmospheres*

I shall first refer to a classical series of observations made by WALDRAM (1945) in moderately clear and in polluted atmospheres, throughout the troposphere, using aircraft, and over the first km of atmosphere by observation balloon. Visual photometry was used in both measurements so that his results cannot be applied to the solar spectrum as a whole. (The solar infra-red contains half the total solar energy (Fig. 1) and absorption in this band may well be greater than in the visible if the particulates contain much water.) The polar diagram of scattered light from a small volume of air was measured at successive heights in the atmosphere and integration of the scatter over all angles gave the scatter coefficient k_s per unit length of air, i.e. $(-1/F)(dF/dx)$ where F is incident flux and dF is the loss of flux by scatter over the path dx. The transmission of energy over an atmospheric depth z when scatter only occurs is then given by $\exp(-\int_0^z k_s dz)$. This was evaluated from $k_s(z)$ using the observations at each level. Simultaneous with the measurement of the polar diagram at height z, the net transmission of the column 0 to z was determined by photometry of an extended illuminated surface at ground level. The difference between this value of transmission and $\exp(-\int_0^z k_s dz)$ provides in principle the absorption by the column. Since k_s is derived from an integration, the error in the inferred absorption could be high but it was not considered to be so high as to make the inference worthless—the absorption was found to be negative at one level on one occasion only, and then insignificantly so.

The observations are not readily summarized so that reference to the original and to the meteorological circumstances is required for a proper assessment. The polar diagrams of scatter, of which examples are shown in Fig. 3 (left) for one occasion, invariably showed a marked excess of forward over backward scatter when the total scatter was not low, and most often too when it was low. Otherwise the forward and backward scatter were about equal. The low values of total scatter occurred, as might be expected, in higher levels, and occasionally near the ground in suitable weather. A minimum generally occurred in the polar diagram at between 90° and 120° to the forward direction of the incident beam, the greater angle going generally with the larger total scatter.

Fig. 3 refers to balloon observations in a very hazy atmosphere to leeward of an industrial town. (Unfortunately no other observations of the pollution are available.) The curves on the right portion are inferred from the polar diagrams and the measured transmissions, and the shaded area, which is the difference between the total scatter and extinction curves, represents the absorption. It will be seen from the polar diagrams that solar radiation in the visible spectrum, falling on this 700 m layer, would have an order of magnitude more energy scattered forward than backward at any level, so that of the 34 per cent scattered by the whole layer from the beam for vertical

incidence (curve on extreme right) most would probably be propagated downward,* and this would be so for any appreciable solar elevation. The absorption by the layer is however considerable, 26 per cent for vertical incidence, as given by the difference between the two right-hand curves at the top of the layer. Most of this absorption occurs in the lower part of the layer, as shown by the hatching. The overall effect of the layer on sunlight would then be to produce significant absorption in the layer at

Curve	Altitude (ft)	k_e
87	0	117×10^{-5}/ft
88	250	$18{\cdot}5 \times 10^{-5}$/ft
89	500	$7{\cdot}5 \times 10^{-5}$/ft
90	1000	$13{\cdot}7 \times 10^{-5}$/ft
91	2000	$13{\cdot}9 \times 10^{-5}$/ft
92	2500	22×10^{-5}/ft

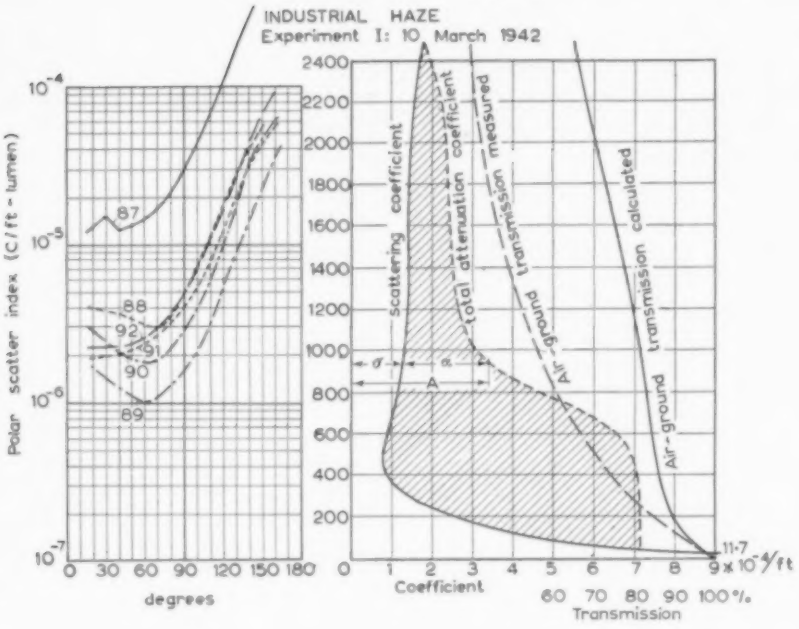

FIG. 3. Curves (left) of intensity of scattered light as ordinate against angle of scatter as abscissa (180° – forward scatter) for different heights above ground to leeward of industrial town, weekday. Note that ordinate is logarithmic.

Curves (right), from left to right, are total scatter coefficient, extinction coefficient, air to ground transmission, and air to ground transmission for scatter only, all as functions of height. The difference between the first two curves is the absorption coefficient, the difference between the second pair the percentage absorption between ground and the level referred. 10 October, 1942. English Midlands. Light wind. Haze top just above 2500 ft. (Reprinted with permission from: J. W. WALDRAM (1945) *Trans. Illum. Engng. Soc.* **10**, 147.)

* But it will be noted (Section 2.3) that we are here in the domain of multiple scattering, so that downward transmission is less than appears from the polar curves. In as far as the sun is not usually obscured by pollution (in the absence of fog) the downward scatter is likely to remain substantial. But see end of next section.

VOL. 1 958/9

the expense of an almost equal absorption at the ground, and to increase somewhat the amount of back scatter from the atmosphere to space.

There is no basis for supposing Fig. 3 to be quite representative of heavy pollution but it should hardly be misleading. The occasion provided the lowest transmission reported by WALDRAM (from a sample of 6) but not the highest scatter coefficients.

2.5 *Observations on solar radiation*

Fig. 4 (top) shows the annual variation, over 6 years (1951–56), of the ratio of daylight illumination on a horizontal surface at a central London site (Victory House, W.C.2) to that at Kew Observatory, Surrey, 13 km WSW of the former site but still within the confines of Greater London. The two sites are thus close enough together to make comparison of pollution effects possible. The daylight illumination is a photometric measure but may be taken as proportional to the energy in visual wavelengths incident on the horizontal surface. It will be seen that the early summer values are within a few per cent of each other, the central London site being the lower, but that in winter the latter site receives 15 to 20 per cent less illumination than Kew. Kew itself, of course, must receive a good deal less illumination than a site in completely rural surroundings with the same cloud and latitude; thus, for example, figures given by STAGG (1950) imply that the total radiation (including solar infra-red) on the horizontal surface with cloudless skies is on average about 15 per cent less than the ceiling values for these occasions. These figures begin to tell one something of the *average* loss in energy received at the earth's surface due to pollution and are not inconsistent with the figures quoted from WALDRAM in the previous section. Again, however, it is to be emphasized that loss of radiation at the earth's surface does not necessarily imply loss of heat to the lower atmosphere since loss at the surface may imply absorption in the air above rather than upward scatter.

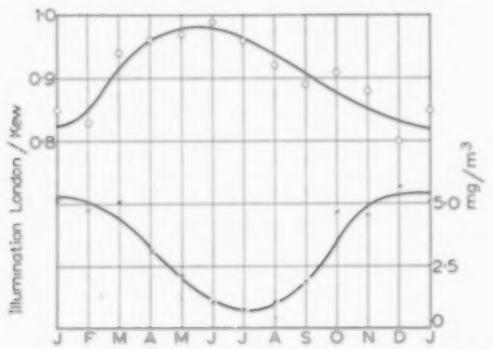

FIG. 4. Upper: Annual variation of ratio of illumination on a horizontal surface in centra London to that at Kew Observatory. Lower: Annual variation of particulate matter in surface air at Kew Observatory from Owen's automatic pollution gauge.

The lower part of Fig. 4 gives the annual variation of surface pollution from an Owen's gauge at Kew Observatory for 5 of the 6 years to which the upper curve relates. The inverse correlation is clear though the retarded phase of the pollution minimum against the maximum of the illumination ratio is perhaps unexpected. In this connexion it is to be remembered that the illumination figures relate to the integral effect

of pollution above the respective stations but the phase difference might be accounted for by more frequent easterlies in the spring than in the autumn.

The above figures relate to average conditions. An example of the effect of a change of wind direction at Kew, from easterly to westerly, on the illumination received from a mainly clear sky on successive days is notable: 586 klm hr on 25 July 1949 and 721 klm hr on 26 July 1949. The 23 per cent increase does not however necessarily reflect the influence of London pollution only on the illumination at Kew. Moreover, the increase in total radiation on the horizontal surface from one day to the next was relatively smaller, from 467 cal/cm² to 506 cal/cm². The difference in behaviour of the two quantities cannot be explained without knowledge of the aerosols and of gaseous absorption.

In line with the London–Kew comparison of illumination are the observations of MEETHAM (1945) on the distribution of solar ultra-violet (3150–3350Å) in and around Leicester over a 2½ year period. He found in winter a minimum in central Leicester, about 25 per cent less than on the outskirts on weekdays and about 20 per cent less on Sundays. There was about 3 per cent difference in summer. The whole Leicester atmosphere was however notably contaminated by pollution from more heavily industrialized areas at about 50 km to the south-west, west and round to north. The absorption or scatter of solar ultra-violet in the given range is of no consequence energetically because of the small amount of energy within the band—it is however of physiological importance. Nor is the measurement of much assistance in inferring the action of pollution on the whole solar spectrum unless reinforced by other spectral measurements or measurement on the particulates.

VOL.
1
958/9

BLACKWELL *et al.* (1954) have made a sophisticated use of observations of solar and sky radiation in clear skies at Kew Observatory in order to estimate the amount of solar radiation which is scattered and absorbed by particulates in the Kew atmosphere. The methods used are too involved to be described here but consist essentially of computing the direct and diffuse solar radiation at ground level, in the visual spectrum and over the whole spectrum, for a model, unpolluted atmosphere. These values are then compared with observed values of the different streams of radiation. It was possible to obtain several more or less independent estimates of the quantities sought and reasonable internal consistency was obtained. As a result the authors infer the following scattering and absorption, as percentages of the extra-terrestrial vertical flux (solar constant = 2·0 cal $cm^{-2}min^{-1}$), in excess of those produced by the pure atmosphere (Table 2):

TABLE 2

Solar elevation (deg.)	54	37	24	12
Additional absorption (per cent)	6	8	11	16
Additional scattering (per cent)	10	10	8	4

Both the additional absorption and scattering were found to be roughly equally shared between the visual and infra-red portions of the spectrum.

The authors' methods were based on an argued assumption that half the scattered light is lost to space so that the last row of figures is to be divided by two to give the energy lost to the earth–atmosphere system by pollution at Kew in clear skies. The

additional absorption is probably spread more or less evenly over the layer in which the pollution is effectively concentrated. It is to be observed that the figures refer to some kind of mean clear atmosphere at Kew, weighted towards the summer months, so that a heavily polluted atmosphere would presumably show much larger additional scatter and absorption. They are not then inconsistent with the figures given in the previous section from WALDRAM.

3. EFFECT OF ATMOSPHERIC POLLUTION ON TERRESTRIAL RADIATION

3.1 *Nature of the radiation and some observations*

The earth's surface emits a flux of black-body radiation upward of amount σT_0^4 (σ is Stefan's constant and T_0 the surface temperature) in the range of wavelength 3 μ to 60 μ (Section 1). This radiation is selectively absorbed by the atmospheric gases, water-vapour, and carbon dioxide in the lower atmosphere and there is background absorption by particulates (the Mie theory is again valid for the latter). The absorbing gases themselves radiate upward and downward in amount proportional to their absorptions in the wavelengths concerned and there is background emission by the particulates, the intensity of the streams increasing with the temperature of the emitters. The overall picture is of a net upward flux of long-wave radiation which varies from level to level in a manner depending on the vertical variation of concentration of the radiatively active constituents and on the vertical variation of temperature. The vertical variation of flux determines a corresponding rate of heating or cooling of the air through which the beam passes; if the flux increases with height there is of necessity cooling; the converse is also true.

Water-vapour and carbon dioxide in realized concentrations are together very strongly absorbent from about 3 μ to 8 μ and upward from about 12 μ so that in these wavelengths the addition of particulate matter is unlikely to affect significantly the flux of radiation in the first kilometre or so of the atmosphere. But between 8 μ and 12 μ, in the so-called atmospheric " window ", particulate matter has the possibility of notably affecting the flux of radiation, for (Fig. 1) it is within these limits that the energy spectrum of the surface flux has its maximum. Thus if particulate matter is strongly absorptive in the window, its own radiation downward will decrease the net upward flux at the surface. Further, its radiation upward at the top of the haze layer will replace in the wavelengths concerned a larger flux originating, in the absence of haze, at the earth's surface which is at the higher temperature for lapse conditions. If there is an inversion through the haze layer—as opposed to one at its top—the net upward flux at the top of the haze layer will be increased by the particulate emission.

It is possible to compute (with some uncertainty) the total downward flux of radiation at the surface from the observed vertical distribution of water-vapour and temperature so that a comparison between this computed flux and the observed downward flux provides in principle a measure of the particulate emission. ROBINSON (1947, 1950) has carried out such comparisons at Kew Observatory for air with visibility better than 1500 km, and has found an excess of observed over computed radiation of about 10 per cent or less, and of order 2 mW/cm^2. In more polluted atmospheres the excess would be greater.

ROACH (1958), observing the solar and atmospheric radiation in the window spectralwise, reached similar conclusions more directly, but the interpretation of the obser-

vations, like ROBINSON's, is not without difficulty. ROACH made his observations both in central London and at Ascot, 40 km to the west. He found that the zenith optical path at $\lambda = 11\ \mu$ ranged from 0·05 to 0·15 at Ascot whereas in London the range was about 0·2 to 0·5, or about three times greater in the mean. As far as the first kilometre or so of the atmosphere is concerned ROACH finds that the non-selective radiation in the window will increase the normal cooling rate of the layer by about 1°C per day at Ascot, and by a good deal more in the strongly polluted air of London. Variations in thermal structure (see above) will also affect the rate of cooling.

3.2 *Computations on a model atmosphere*

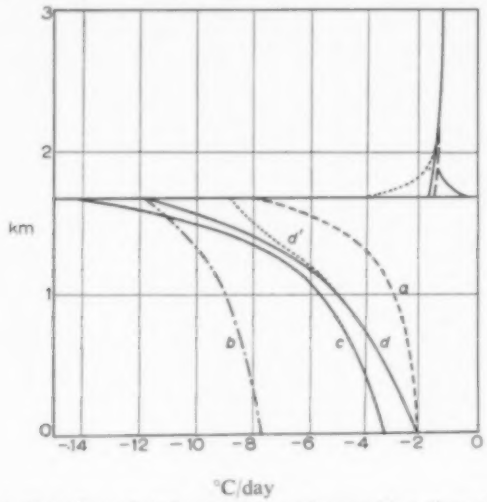

FIG. 5. Computed rates of cooling of air in and above a layer with a discontinuity in water-vapour or haze or both at the top of the layer.

(a) Water-vapour only
(b) Haze only
(c) Water-vapour + haze
(d) As (c) for isothermal atmosphere
(d') As (d) for 2°C inversion at haze top

(Reprinted with permission from: F. MÖLLER (1941) *Die Warmestrahlung des Wasserdampfes in der Atmosphäre* s. 33. Akademische Verlagsgesellschaft, Leipzig.)

In the light of the above observations it is of interest to refer to computations made by Möller (1941) on the effect of a haze layer on the radiative cooling of the air. Fig. 5 shows the results of the computations which were made on the following basis:

Surface temperature	10°C
Haze-top at	1·67 km
Relative humidity in haze	100 per cent
above haze	20 per cent
Dust concentration in haze,	proportional to vapour concentration, i.e. concentration at haze top half surface concentration. Mean 1000/cm³ of $d = 1\ \mu$.
above haze	zero
Curves (a), (b), (c):	Lapse rate = 6°C/km (a) water-vapour (b) haze (c) water-vapour and haze

VOL. 1 958/9

Curve (d):	As (c) for isothermal atmosphere
Curve (d′):	As (d) but with inversion of 2°C at haze top
Absorption coefficient of haze (grey body):	$0{\cdot}7 \times 10^{-4}\text{cm}^{-1}$

Comparison of curves (a), (b), (c) for water-vapour alone, haze alone, and water-vapour + haze respectively shows that haze is a more effective coolant than water-vapour and that combined with water-vapour it increases the cooling rate by from 1°C per day near the base to 6°C or 7°C per day near the top of the layer. The effect of thermal stratification, as shown by comparing curves (c) and (d), is not very great and the realistic inclusion of an inversion at the haze top lessens the cooling somewhat beneath the top of the haze and increases it correspondingly above the haze top. The overall effect of the haze in the isothermal atmosphere with inversion is to increase the cooling rate by about 2°C per day at most levels within and immediately above the haze. The computations were made when radiation theory was less developed than at present, but they probably provide correct order of magnitude values of the effects discussed.

4. INTEGRATION OF EFFECTS

It would now be desirable to make a comprehensive assessment of the effects of pollution on the solar and terrestrial beams jointly, in regard to the total energy transformations in the polluted air. This can not yet be done for reasons which are apparent in previous sections but some drawing together of ends is indicated.

The reader is first reminded that the effects of pollution on solar radiation are confined to the daylight hours—for practical purposes when the sun is above 5° elevation, because there is negligible solar energy incident on the extra-terrestrial horizontal surface at lower elevations—whereas the effects on terrestrial radiation are present throughout every 24 hr, though there may be some diurnal variation through changes in temperature structure.

Dealing first with scatter, this has been shown to be significant for the solar beam and results by upward scatter in a loss of energy to the air–earth system of order, perhaps 20 per cent of the extra-terrestrial flux in notably polluted air. The relative loss is greater the lower the solar elevation. Some additional energy is subtracted from the solar beam and added to the downward diffuse (sky) radiation. Pollution also undoubtedly scatters terrestrial radiation but the effect is of no material consequence to the net flux of this radiation.

Turning now to absorption, this has been shown to be significant for both solar and terrestrial beams but the effects on the temperature of the air and of the ground are in opposite sense for the two beams. Absorption of the solar beam produces heating of the air which might amount to 1 or 2°C per day when the mid-day sun has appreciable elevation and this would be spread more or less uniformly over the haze layer. There would be a corresponding loss of heat to the ground, the pollution taking the place of convection in transmitting heat upward through the haze layer. The absorption and associated emission of terrestrial radiation by particulate pollution appears to be capable of cooling the air over the haze layer by a few °C per day but there would be rather less cooling of the ground surface under a diminished net upward flux of radiation from the ground. The bad cases of pollution occur of course in general in the winter when solar absorption is necessarily low and the cooling by terrestrial

radiation would then dominate. To this has to be added the loss of solar radiation by upward scatter.

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VOL.
1
958/9

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COALESCENCE OF DROPLETS IN AQUEOUS-DISPERSE AEROSOLS

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Abstract—It has been suggested that coalescence between droplets in artificial fogs, prepared from aqueous electrolyte solutions, may be influenced by the structure of the electrical double layer in the surfaces of the droplets. In this paper coalescence between unlike droplets has been studied in a mixed fog, prepared from two electrolyte solutions, which react to give a coloration. Such coalescence has been found to be dependent upon solution concentration and a marked effect of added surface-active agents has been demonstrated. The experimental results may be qualitatively explained on the basis of the ion distribution in the surfaces of the droplets.

INTRODUCTION

In recent years the problem of the dispersal and precipitation of suspended aqueous droplets has received much attention, especially in the field of meteorology, and considerable interest has been roused over the relative importance of droplet–droplet coalescence and evaporation–condensation mechanisms (Bowen, 1950; Ludlam, 1951; Squires, 1951).

More recently it has been demonstrated (Elton *et al.*, 1956; Benton and Elton, 1957; Griffiths, 1957) that, in artificial fogs produced by solution atomization processes, the stability of the fog was dependent upon electrolyte concentration of the atomized solutions. Results indicated that the rate of growth of the droplets in the fog was dependent upon electrolyte concentration.

The droplet growth process may be considered to result from two types of mechanism:

(1) Evaporation–condensation. Distillation of water-vapour takes place from small to large droplets (Kelvin effect). Increased electrolyte concentration will reduce the process because of the lowered water-vapour pressure over the droplets and the consequent change in the rate of distillation.

(2) Droplet coalescence. Whether or not collision of two droplets leads to coalescence may be dependent on repulsive forces between them, arising from the electrical double layers in their surfaces. The structure of these double layers would be dependent on electrolyte concentration.

It should be mentioned that both of these mechanisms may operate in conjunction with a basic condensation of water, from the saturated air, on to the droplets (Prokhorov *et al.*, 1957). This will increase with electrolyte concentration and will tend to render the fog more homodisperse, thus conferring relatively greater stability upon fogs produced from more concentrated solutions, due to a reduction in both differential settling and Kelvin effects.

The evaporation–condensation processes mentioned above are well known. However, the theoretical treatment of neither of these processes nor the electrical double

layer inside a droplet is sufficiently advanced to allow a definite decision to be taken as to which has the dominant effect upon fog stability.

The present work was undertaken in an attempt to obtain direct evidence for the occurrence of droplet coalescence and of any dependence of such coalescence upon electrolyte concentration and electrical double-layer structure in the droplet surfaces.

A simple method of detecting coalescence was employed, using two solutions which when mixed gave an intense red coloration. A mixed fog, generated by atomization of the two solutions was prepared and examined for red coloured droplets, which could only have arisen by coalescence of droplets of one solution with those of the other. These experiments differed from those mentioned above (ELTON *et al.*, 1956; BENTON and ELTON, 1957; GRIFFITHS, 1957) in that the coalescence investigated was between dissimilar droplets, but the effect of such factors as electrolyte concentration could be studied and comparisons drawn with the earlier experiments.

APPARATUS AND MATERIALS

The fog chamber consisted of a rectangular box, 4 ft high and 1·5 ft × 2 ft in cross-section, constructed from water-proofed fibre board with a steel frame. Access to the interior was by means of a door which formed the whole of one side. When necessary the chamber could be divided into two separate compartments, one above the other, by inserting a horizontal sliding partition. Four inches above the floor of each compartment provision was made for a glass microscope slide to be inserted from outside, exposed to the fog for a suitable time, and removed again, all with the minimum disturbance to the fog.

VOL.
1
958/9

Fogs were prepared using glass atomizers, operated by an air blast at 10 lb/in². The air supply was first passed through a column of distilled water in an attempt to presaturate it. Two such atomizers were employed, one for each solution, and mounted so that the discharge was directed through small holes into the chamber, one at the upper compartment and one at the lower compartment.

Solutions used were ammonium or potassium thiocyanate and ferric ammonium sulphate. These were prepared from Analar grade materials in distilled water, the ferric solution being acidified with a known amount of sulphuric acid to prevent hydrolysis. Coalescence of a droplet of a thiocyanate solution with one of ferric solution resulted in a red coloured droplet, due to formation of ferric thiocyanate. Although this coloration is intense even in great dilution, it was found difficult to detect the colour in micron-sized droplets. Experiment showed that only when the solution concentrations were 0·1 N or greater could the coloured droplets be distinguished with certainty. In this work, therefore, such concentrations of solutions were used.

The fogs were sampled by allowing the droplets to settle under gravity on to a microscope slide thinly coated with Vaseline. The deposit was then examined with a microscope equipped with a × 12 eyepiece and a 4 mm 0·85 N.A. objective, the combination giving a linear magnification of about 530. Droplet sizing was carried out in the standard way (FAIRS, 1943) using a modified Fairs' graticule mounted on the eyepiece, this having been accurately calibrated with a standard graduated slide mounted on the microscope stage.

The purpose of coating on the slide was to make the surface hydrophobic and to ensure that the droplets collected retained their spherical shape. The normal dis-

advantage with this method of collection, i.e. that droplets evaporate and disappear when the slide is removed from the saturated atmosphere for examination, did not apply in this case because of the amount of electrolyte contained in the droplets. Sampled droplets from fogs made from solutions 0·1 N or greater were found to be practically unchanged in size after standing exposed in the laboratory for 30 min.

The use of Vaseline was found to be important since preliminary tests indicated that other materials (e.g. Spirax gear oil, 230—an oil frequently used for droplet collection) either masked the colour of the red droplets or imparted a spurious red coloration to droplets of thiocyanate solutions, presumably because of the presence of iron impurities. Vaseline possessed neither of these disadvantages.

EXPERIMENTAL PROCEDURE

Preliminary experiments were carried out to determine the most satisfactory procedure to be adopted in fog preparation and sampling.

The dividing partition was omitted, the chamber well washed down internally with water and left for some time to allow the air inside to become saturated. The two sprays, one containing ferric solution, the other thiocyanate solution, were started simultaneously using the same air pressure, 10 lb/in², and operated for 2 min. The resultant fog was left undisturbed for a measured time and then the sampling slide inserted near the bottom of the chamber for a measured time. This was subsequently examined for coloured droplets.

The period during which the fog was left undisturbed after spraying allowed turbulence to die away. If this was not allowed the fraction of the slide area covered by droplets varied considerably from experiment to experiment. A period of 5 min was found sufficient for satisfactory reproducibility.

The period for which the slide was exposed to the fog obviously controlled the number of droplets sampled. A high surface coverage introduced complications mentioned below. This was therefore avoided and exposures of 1 min were adopted as most satisfactory, giving fractional surface coverages not greater than approximately 0·02.

The effect of electrolyte concentration upon droplet coalescence was investigated in two systems. In the first, the electrolytes used were ferric ammonium sulphate and ammonium thiocyanate, the concentration of the former being varied. In the second the electrolytes used were ferric ammonium sulphate and potassium thiocyanate, the concentration of the latter being varied.

Further studies were made in which surface-active agents were added to one or both of a 1 N solution of ammonium thiocyanate and a solution 0·5 N with respect to both ferric ammonium sulphate and sulphuric acid. Agents employed were " Benzalkonium chloride " (BAC) (a Leda Chemicals product consisting of mixed alkyl dimethylbenzyl ammonium chloride) and " Teepol " (a Shell Chemicals product; an anionic agent).

Droplet size distributions were determined for the different mixed fogs prepared. These did not differ significantly from one another. Ninety per cent of droplets sampled lay in the range 1–5 μ diameter with mean diameter of approximately 3 μ.

An important point to be considered is the possibility that some of the coloured droplets in a sample were produced not in the fog, but by superposed collection of unlike droplets on the slide.

It has been shown (PICKNETT, 1958) that the number of coalescences, n, which occur on the sampling slide, by superposed collection, per unit area is given by:

$$n = N + \{(1 - Na) \ln (1 - Na)\}/a$$

where N = total number of droplets per unit area
$a = \pi d^2/4$
d = droplet diameter

The equation applies, strictly, to a monodisperse fog but satisfactory agreement with results in the case of fogs now under discussion has been obtained. The equation was tested experimentally. The fog chamber was divided by the horizontal sliding partition and fogs prepared from thiocyanate solution in the upper compartment and ferric solution in the lower compartment. A sampling slide was exposed first to the one fog and then immediately to the other. The proportion of coloured droplets on the slide (these could only have been formed by superposed collection) was determined and compared with that calculated from the above equations. Satisfactory agreement was obtained for fractional surface coverages ranging from 0·003 to 0·03.

In the case of samples taken from mixed fogs the result is obtained that, for a fractional surface coverage of 0·02, only 0·5 per cent of the sampled droplets were coloured due to superposed collection.

TABLE 1

Solution 1	Solution 2	% coloured droplets in sample	Standard deviation from the mean
1N NH_4CNS	0·1N w.r.t. Fe Alum 0·1N w.r.t. H_2SO_4	11·1	1·4
1N NH_4CNS	0·5N w.r.t. Fe Alum 0·5N w.r.t. H_2SO_4	14·6	1·6
1N NH_4CNS	2·0N w.r.t. Fe Alum 0·5N w.r.t. H_2SO_4	18·6	1·7

TABLE 2

Solution 1	Solution 2	% coloured droplets in sample	Standard deviation from the mean
0·1N KCNS	0·5N w.r.t. Fe Alum 0·5N w.r.t. H_2SO_4	2·0	0·6
0·5N KCNS	0·5N w.r.t. Fe Alum 0·5N w.r.t. H_2SO_4	6·5	1·1
1N KCNS	0·5N w.r.t. Fe Alum 0·5N w.r.t. H_2SO_4	16·0	1·5
2N KCNS	0·5N w.r.t. Fe Alum 0·5N w.r.t. H_2SO_4	20·3	2·0

RESULTS

Results shown in Tables 1 and 2 indicate a dependence of the proportion of droplets undergoing coalescence upon the concentration of the solutions sprayed. It is seen that as the concentration of either the ferric solution or the thiocyanate solution is increased the proportion of droplets undergoing coalescence is increased.

VOL. 1 958/9

Results shown in Tables 3 and 4 and Figs. 1 and 2 illustrate the effect of added surface-active agents. The cationic agent (BAC) is seen to promote formation of coloured droplets when in the ferric solution and to inhibit their formation when in the thiocyanate solution; the reverse effect is seen in the case of additions of the anionic agent Teepol.

Table 3

Solutions: (1) 1N NH_4CNS
(2) 0·5N w.r.t. Fe Alum
0·5N w.r.t. H_2SO_4

Surface-active agent added to Fe solution	Concentration of surface-active agent (p.p.m.)	% coloured droplets in sample	Standard deviation from the mean
BAC	1	17·6	2·6
BAC	10	18·5	1·4
BAC	50	20·0	1·6
Teepol	1	12·2	1·6
Teepol	10	9·9	1·6
Teepol	50	8·0	1·3

Table 4

Solutions: (1) 1N NH_4CNS
(2) 0·5N w.r.t. Fe Alum
0·5N w.r.t. H_2SO_4

Surface-active agent added to thiocyanate solution	Concentration of surface-active agent (p.p.m.)	% coloured droplets in sample	Standard deviation from the mean
BAC	1	10·5	1·1
BAC	10	7·8	1·4
BAC	50	7·0	1·3
Teepol	1	17·7	2·0
Teepol	10	17·3	1·7
Teepol	50	18·9	1·6

Each recorded percentage of coloured droplets is the mean of at least eight experiments. Standard deviations of individual results from the means are indicated

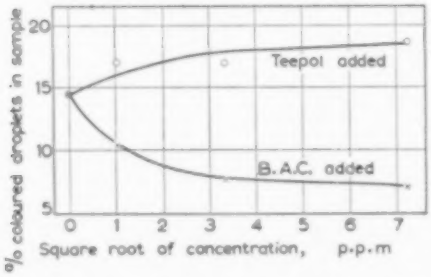

Fig. 1. Surface-active agents added to the iron solution.

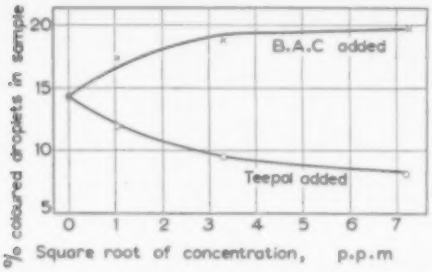

FIG. 2. Surface-active agents added to the thiocyanate solution.

DISCUSSION

The results in Tables 1 and 2 establish the fact that coalescence of droplets containing ferric ions with droplets containing thiocyanate ions is promoted by increased concentration of either ion. The critical nature of the sign of the surface-active ion added to the electrolyte solutions, as illustrated in Tables 3 and 4, suggests that this coalescence is markedly influenced by an electrical effect associated with the presence of ions at the droplet surfaces. Indeed, a reasonable explanation of the experimental data can be based on the known properties of ions at an air–water interface.

It is well known from surface-tension measurements that simple ions are repelled from the air–water interface (LANGMUIR, 1917). Early work (FRUMKIN, 1924) on surface potentials showed that cations and anions had, in general, different degrees of negative adsorption, resulting in an unequal distribution of charges near the surface. For 1–1 type electrolytes the anions exhibit the least negative adsorption, so that the region near the surface becomes negatively charged with respect to the interior of the liquid. Recent work (RANDLES, 1957) has shown that this surface charge becomes greater with increasing electrolyte concentration and that certain anions (including the thiocyanate ion) produce a very marked effect.

We have previously suggested (BENTON and ELTON, 1957) that, when two similar droplets of water or aqueous electrolyte solution approach one another, the similar orientation of charge in the surfaces of the droplets might lead to a repulsion between them, at close approach, thus opposing coalescence.

BACH and GILMAN (1938) studied the electrophoresis of air bubbles in aqueous electrolyte solutions and showed that the sign of the surface charge, in solutions of 1–1 type electrolytes is negative. In the present experiments the droplets of ammonium or potassium thiocyanate solutions would be expected to possess a negative surface charge. But the coalescence studied is between unlike droplets. The droplets of ferric solution might be expected to possess a positive surface charge due to preferential adsorption of the tervalent ferric ion. This assumption is in fact supported by the work of BACH and GILMAN (1938) who found that the sign of the charge at the surface of air bubbles in solutions of thorium chloride of concentration greater than 0·00001 N was positive.

The opposite surface charges on the two types of droplet would tend to cause an attraction at close approach of unlike droplets. Furthermore, an increase of concentration, producing an increased surface charge, might thus be expected to cause increased attraction and coalescence between unlike droplets. This is in fact the result observed.

VOL.
1
958/9

The results obtained with surface-active agents added to the solutions provide further support for this theory. Addition of cationic agent to the ferric solution will tend to increase the positive surface charge on these droplets and addition of anionic agent to the thiocyanate solution will likewise tend to increase the negative surface charge. In either case increased attraction and coalescence between unlike droplets would be expected and is observed. Conversely, addition of cationic agent to the thiocyanate solution or of anionic agent to the ferric solution would tend to decrease and subsequently reverse the respective charges on the droplet surfaces. In both of these cases reduced attraction, or repulsion, between unlike droplets and hence decreased coalescence would be expected, as is again found to be the case.

It may be noted further that when cationic agent (50 p.p.m.) was added to the ferric solution, and at the same time, anionic agent (50 p.p.m.) was added to the thiocyanate solution, the greatest observed proportion of coloured droplets (23·5 per cent) was obtained.

It is to be emphasized that the results given here for the proportion of coloured droplets apply to the samples collected on the slide. It is not possible at present to assess quantitatively the effect of electrolyte concentration on the coalescence efficiency for droplets colliding in the fog. There are two main reasons for this:

(1) Factors which promote coalescence between unlike droplets will discourage coalescence between like droplets.
(2) Coalesced droplets will, on average, be larger than droplets which have not coalesced and will therefore be sampled preferentially.

Nevertheless this work demonstrates that coalescence between droplets definitely occurs in the fogs under the turbulent conditions which obtained during spraying and the fact that the theory provides a qualitative explanation of the experimental data is strong support for the conclusion that this coalescence is markedly affected by the electrical forces arising from the distribution of ions in the droplets.

VO
1
1958

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THE APPLICATION OF PHENOLPHTHALIN REAGENT TO ATMOSPHERIC OXIDANT ANALYSIS

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Abstract—In recent years, a form of air pollution has developed which is characterized by a strong oxidizing effect. For the measurement of this effect a colorimetric method has been developed, based on the oxidation of phenolphthalin to phenolphthalein. Good correlation has been reported between oxidant determined by this method and subjective observation, and a comparison is made of data obtained by different methods.

A simple, semi-automatic sampler is described, and the results of 5 years of continuous sampling are presented.

AIR pollution problems caused by photochemical oxidation of organic material in the presence of oxides of nitrogen, first noted in Los Angeles, are associated with eye-irritating haze, objectionable odor and plant damage (HAAGEN-SMIT *et al.*, 1953). These characteristic manifestations are physiological in nature, and their intensity at different times and locations are difficult to compare unless we possess an objective chemical or physical method by which this intensity can be measured. Early investigations had shown that one of the most outstanding characteristics of the Los Angeles smog is its strong oxidizing effect. This effect is due to the presence of a number of compounds, each of which possesses oxidative capacity. The most important of these are:

(a) Ozone
(b) Nitrogen compounds, such as nitrogen dioxide, alkyl nitrites, and peroxy alkyl nitrites
(c) Peroxides of many types, formed in the oxidation of organic material.

The last group is held mainly responsible for the irritating action of smog. Directly linked with the formation of these peroxidic products is ozone, which constitutes a major part of the oxidant during smog periods. Since the oxidant comprises substances involved in reactions leading to the irritants, in principle, any substance which is readily oxidized can serve as a measure of smog conditions.

We have demonstrated the effect of smog on biochemically important compounds such as the amino acids cysteine and glutathione and the enzyme, lysozyme. The latter compound, especially, is important because of its relation to eye irritation which has often been correlated with the activity of lysozyme. Other reagents responding to the action of oxidant are ferrous thiocyanate, indigosulfonic acid, fluorescein, methylene blue, bixin, rubber, titanium sulfuric acid, iron pentacarbonyl, lead tetracetate, cobaltostearate, potassium iodide and phenolphthalin (EGGERSGLÜSS, 1951). For a routine determination potassium iodide and phenolphthalin react with sufficient speed to be used for atmospheric sampling. Several methods for air analysis, based on the liberation of iodine from potassium iodide have been described (SMITH and DIAMOND,

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VOL.
1
958/9

1952; RENZETTI and ROMANOVSKY, 1956). This method has been adapted to continuous automatic sampling (LITTMAN and BENOLIEL, 1953) and is also frequently used for spot analysis for oxidants. Potassium iodide is rather sensitive to atmospheric oxygen, and the relatively large volume used in sampling may result in considerable blank values. In addition, it often happens that the reagent before use, or in its preparation, is already contaminated with free iodine. While all these objections can be overcome by careful technique requiring skilled labor, for field work it is often not possible to take proper precautions.

A procedure originally proposed by SCHALES for determining hydrogen peroxide in biological preparations (SCHALES, 1938) overcomes some of these objections, and attempts were therefore made to apply this method to atmospheric sampling. The test is based on the oxidation of phenolphthalin to phenolphthalein, according to the following equation:

$$\underset{\text{phenolphthalin}}{C_{20}H_{16}O_4} \xrightarrow[\frac{1}{2}O_2]{H_2O_2} \underset{\text{phenolphthalein}}{C_{20}H_{14}O_4}$$

The method is quite sensitive to a variety of oxidizing agents present in the Los Angeles air, and with only a few liters of smog air an intense reddish-purple color is produced. There is little interference by atmospheric oxygen, and the intense color developed affords the possibility of a visual comparison with color standards.

REAGENTS

Phenolphthalin. One g of phenolphthalein, with 10 g of sodium hydroxide, 5 g of zinc dust and 20 ml of distilled water are warmed in a flask equipped with a reflux condenser over a water bath for approximately 2 hr, until colorless, then filtered through a sintered glass filter and diluted with 50 ml of distilled water. This concentrated reagent is stored over granulated zinc in a closed bottle, in the dark, preferably under refrigeration.

Copper sulfate. 0·01 M in distilled water. Dissolve 2·497 g $CuSO_4 . 5 H_2O$ in 1 l. of distilled water.

TEST PROCEDURE

One ml of the concentrated phenolphthalin reagent is diluted with 3·0 ml of distilled water. To 100 ml of distilled water is added 1·0 ml of the dilute phenolphthalin reagent and 0·5 ml of the copper sulfate solution. After thorough mixing, this reagent is used for the test.

Ten ml of the test reagent is placed in a bubbler (see Fig. 1), and air is passed through at 900 ml/min for 10 min.* Any color developed is read in a Klett–Summerson

* Tygon tubing has been found to give a positive peroxide reaction. It is therefore important to avoid the use of Tygon on the inlet side of the bubbler. Rubber, because of its reaction with ozone, should also be avoided. We recommend glass-to-glass connections on the inlet, preferably with ground joints (Fig. 1). In order to obtain atmospheric samples, while housing the machine within the laboratory, we have made use of extended sampling tubes measuring approximately 4 ft in length by 8 mm i.d. These tubes can be extended through an open window and connected to the bubbler by means of a 18/7 TS ball and socket ground glass joint. We have found that such an arrangement affords a barrier against further contamination by atmospheric pollutants. The flow meter is placed between the outlet side of the impinger and the suction pump.

VOL.
1
958/9

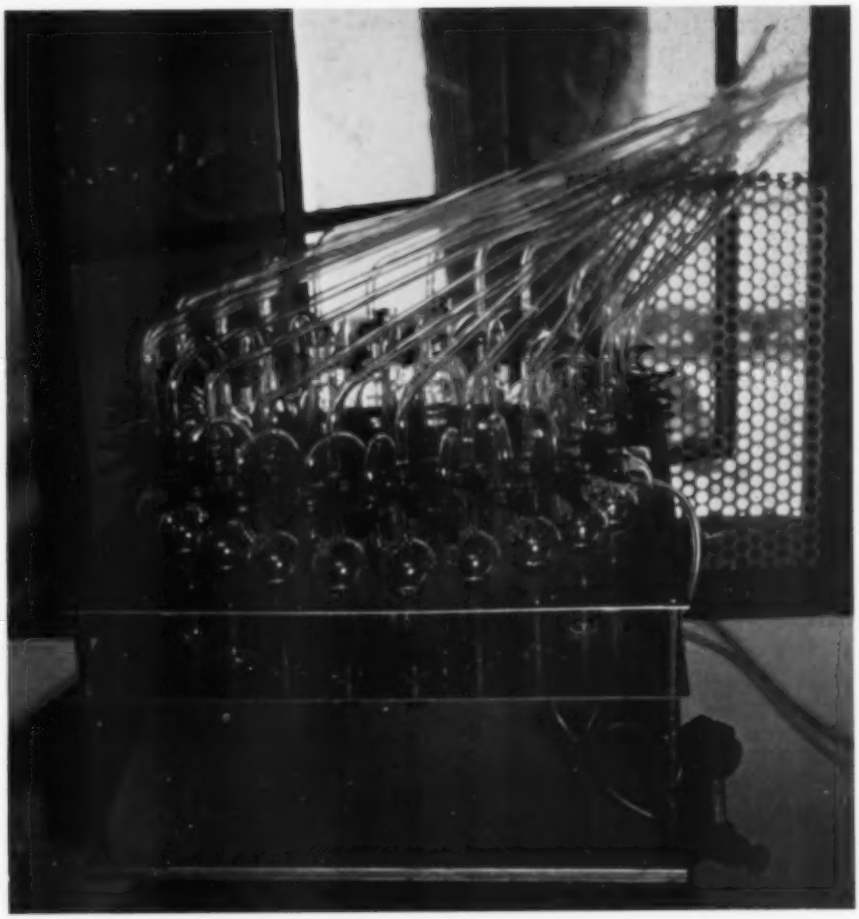

FIG. 1. Automatic sampling machine.

VO
1
1958

colorimeter, using a green filter (No. 54). The concentration of the oxidant can be estimated from a standard curve.

STANDARD CURVE

Dilutions of 30 per cent hydrogen peroxide were made, and 10 ml portions of the diluted solutions were treated with 0·1 ml of dilute phenolphthalin and 0·05 ml of copper sulfate reagents. After 15 min the color developed was read in a Klett–Summerson colorimeter, using the Klett green filter (No. 54). Concentration of hydrogen peroxide was plotted against the colorimeter reading corrected for the blank, and the reading expressed as p.p.m. hydrogen peroxide. The calibration with ozone of known concentration is cumbersome, and is not preferred for routine test. The oxidant value obtained from H_2O_2 standardization can be converted to ozone values by dividing by two.

BLANK

Generally the unaerated blank was found to be relatively constant at 10 ± 3 on the colorimeter scale. High blanks are sometimes encountered during hot weather unless precautions are taken to keep the reagents cool. All colorimeter readings were corrected for the blank in plotting the standard curve and in subsequent readings. Each fresh batch of reagent was standardized before use.

EFFECT OF TIME ON COLOR DEVELOPMENT

In spot analyses the purple color of the phenolphthalein is read after 10–15 min when the color has reached a maximum intensity. After longer standing, the color developed with H_2O_2 fades slightly. After 8 hr the color intensity is reduced by 10 per cent at the 0·5 p.p.m. level. At lower oxidant concentrations this is proportionately less.

In actual practice of atmospheric sampling, the color produced by oxidants continues to develop slightly over a period of ½–1 hr, probably due to slow reaction of some of the organic peroxides. Fading and increase in color tend to counteract each other, and we found it satisfactory to evaluate at the end of each day all the samples collected hourly.

COMPARISON OF PHENOLPHTHALIN METHOD TO OTHER OXIDANT REAGENTS

Calibration of the reagent against known concentrations of ozone shows that 1 p.p.m. of active oxygen, as indicated by standardization with H_2O_2, is equivalent to ½ p.p.m. of ozone. This relation has been confirmed in a comparative study of Los Angeles oxidant measurements obtained by several investigating groups, which was presented by RENZETTI and ROMANOVSKY (1956).

In many years of sampling with potassium iodide, phenolphthalin and rubber, we have found that the figures obtained with each one of these methods increase during smog periods. An example of data obtained on a moderate smog day using all three methods of sampling is shown in Table 1.

It is apparent that during the smog hours the phenolphthalin ozone values are somewhat higher and remain higher for a longer period than ozone indicated by either potassium iodide or rubber cracking. This behavior is more pronounced on severe smog days.

VOL.
1
958/9

TABLE 1. COMPARISON OF KI (PHOSPHATE BUFFER), RUBBER CRACKING, AND PHENOLPHTHALIN ON A SMOG DAY (6 NOVEMBER 1953)

Potassium iodide		Rubber		Phenolphthalin			
Time	Ozone (p.p.m.)	Time	Ozone (p.p.m.)	Time	Total oxidant (p.p.m.) Calculated as H_2O_2	Calculated as O_3	PP (O_3) KI (O_3)
				8.40–8.50	0·12	0·06	
9.50–10.40	0·10	10.13–11.13	0·10	9.40–9.50	0·18	0·09	0·9
10.50–11.40	0·14	11.15–12.00	0·10	10.40–10.50	0·24	0·12	0·9
11.50–12.40	0·20	12.00–12.30	0·19	11.40–11.50	0·45	0·23	1·2
		12.30–12.45	0·25				
12.50–1.20	0·25	12.48–12.58	0·25	12.40–12.50	0·58	0·29	1·2
		12.59–1.15	0·22				
1.50–2.40	0·11	1.17–1.37	0·19				
		1.41–2.00	0·16	1.40–1.50	0·45	0·23	2·1
2.50–3.40	0·07	2.12–3.12	0·05	2.40–2.50	0·26	0·13	1·9
		3.15–5.00	0·04				
				3.40–3.50	0·16	0·08	
				4.40–4.50	0·10	0·05	

During the period from 1 February 1957 through 31 May 1957, there were 49 days of moderate to severe smog (total oxidant by phenolphthalin method 20 p.p.h.m.), and 27 days of lower oxidant values, on which ozone was determined both by rubber cracking and with phenolphthalin reagent. On smog days the ratio of O_3 (by phenolphthalin) to O_3 (by rubber cracking) is $2{\cdot}3 \pm 0{\cdot}7$, whereas this ratio is $1{\cdot}0 \pm 0{\cdot}3$ during non-smog days.

A similar phenomenon was shown in 1951 when a comparison was made of ozone determined by the rubber cracking method and organic peroxides determined by the development of blue color with gum guiaic in the presence of peroxidase during a severe smog attack (HAAGEN-SMIT, 1952). Here, too, it was observed that the ozone concentration decreased rapidly while the peroxide value remained high for an additional period of approximately 1 hr.

The oxidant as measured with phenolphthalin and potassium iodide is the resultant action of several oxidizing materials—ozone, nitrogen dioxide and a variety of peroxides. In some areas these reactions are neutralized by the presence of reducing agents, especially SO_2. Ozone reacts rapidly with phenolphthalin reagent, and very little is caught in a second trap. Both oxides of nitrogen and organic peroxides react much more slowly, and we find during intense smog periods the second and third bubbler still reacting. A true measure of the smog would involve a correction for the non-eye-irritating ozone and nitrogen dioxide. What is left after such a correction would represent organic peroxides. Unfortunately, the different types of peroxides react at different rates; some of them, such as dialkyl peroxides, have no perceptible reaction. For practical purposes in monitoring smog conditions, the uncorrected values correlate sufficiently well with subjective observation, that they can be used

VOL.
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58/9

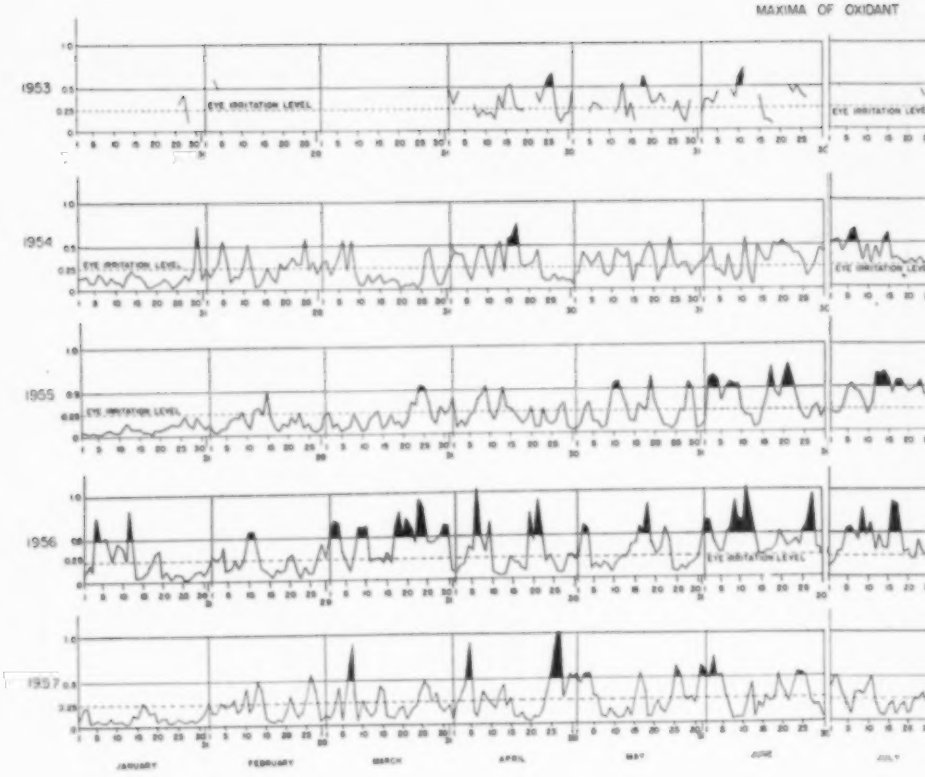

FIG. 4. Daily oxidant maxima, 19

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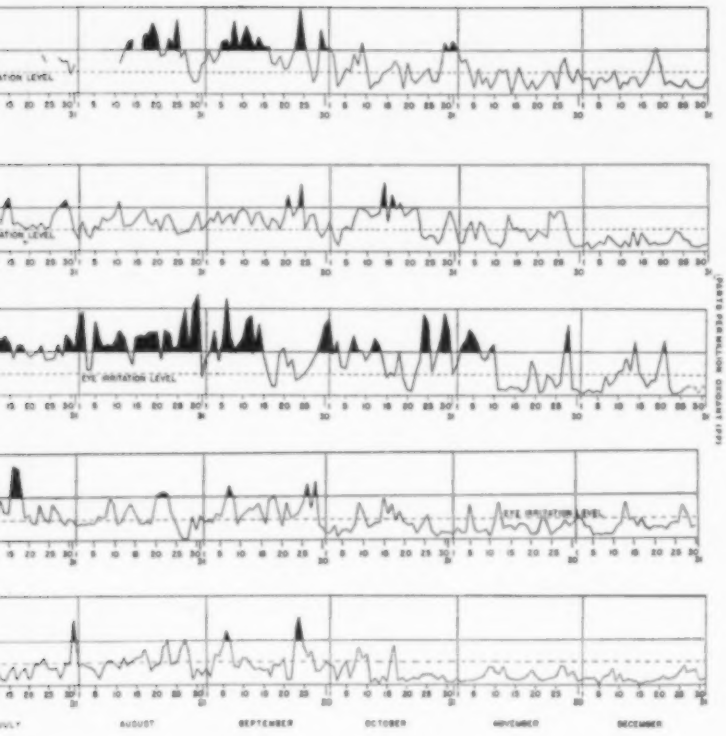

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directly, and over a period of years the oxidant concentrations reported below for the perception of odor, eye irritation and severe smog, have remained quite consistent.

One of the advantages of the phenolphthalin method is that little skill or equipment is necessary for its application to field sampling. In that case, solutions which are prepared on the spot can be compared directly with standards based on water dilutions of a solution of fuchsin dye in alcohol which have nearly the same color as the phenolphthalin reagent, and have been previously calibrated on the photometer. It is possible to estimate differences in these standards equivalent to 0·06 p.p.m. of oxidant.

In our field work we have used two 10 l. bottles, one filled with water, as a pump. The 10 l. sample is drawn through the reagent by suction caused by siphoning the water from one bottle to the other. In these field tests the use of the automobile or Diesel engine as a power supply is to be avoided, for it has been our observation that large amounts of oxides of nitrogen may be formed and contaminate the atmosphere.

In planning for an extended period of atmospheric sampling, an automatic sampling machine was designed and built at our laboratory which takes one 10 min sample each hour over a 24 hr period. The machine, which has operated faithfully for 5 years, is shown in the accompanying photograph. It consists of a series of bubblers connected to a manifold designed in such a way that a sample of air is drawn through each bubbler in turn. A very satisfactory pump for this purpose is manufactured by the Redmond Company, Inc., Owosso, Michigan, their motor Model No. 3354, Type L, 115 V, h.p. 1/70, 1550 rev/min, coupled to their Dyna Pump, Model 2. This pump provides quiet, dependable service, and has more than enough capacity for our sampling. A ratchet arrangement rotates the upper part of the manifold according to a timed program, thereby connecting each bubbler in turn to the vacuum pump. The duration of the sampling time may be varied at will by redesigning the cams. The wiring diagram is shown in Fig. 2, and a description of the operation of the timer unit follows:

VOL.
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958/9

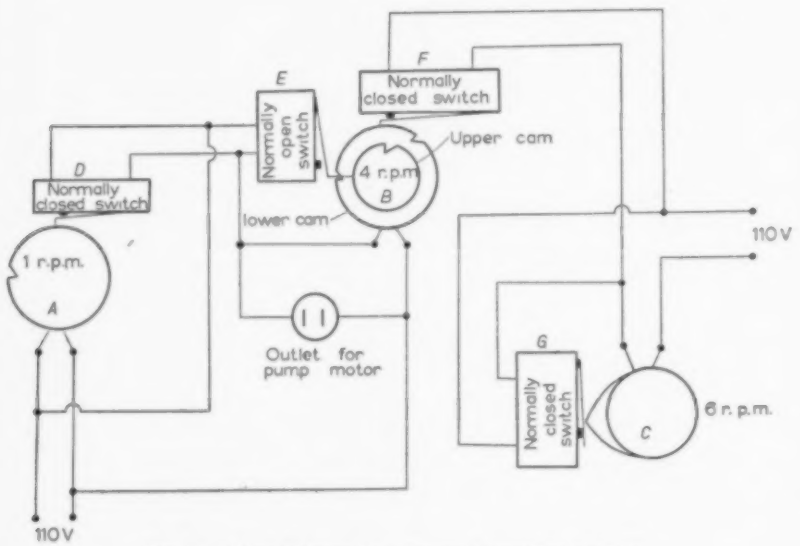

FIG. 2. Wiring diagram for automatic sampling machine.

Operation of timer unit

(1) Manually turn on 1 RPH Motor (*A*).
(2) Once every hr switch (*D*) will close, starting motor (*B*) and pump motor.
(3) Switch (*E*) closes as (*B*) turns, so taking over for switch (*D*) which opens after some time.
(4) As the 4 RPH motor (*B*) turns, switch (*F*) is closed, starting motor (*C*).
(5) Motor (*C*) turns, bringing the 48 position valve to one of its open positions and closing switch (*G*). Meanwhile switch (*F*) is closed by motor (*B*).
(6) After motor (*C*) has turned one revolution and completed the opening of the valve, it is turned off by switch (*G*).
(7) Motor (*B*) continues to turn, and 10 min after step 6, switch (*F*) is again closed, steps 5 and 6 are repeated.
(8) Motor (*B*) turns until switch (*E*) opens, turning off the pump and motor (*B*).
(9) When motor (*A*) causes switch (*D*) to close again, the complete cycle is repeated.

RESULTS

For an extended period of time, subjective observations on odor, as well as eye irritation were recorded and compared to phenolphthalin oxidant values. We found that when the total oxidant reached a level of 0·15 p.p.m., calculated as H_2O_2, smog odor is apparent; at a level of 0·25 p.p.m. eye irritation is generally experienced, and

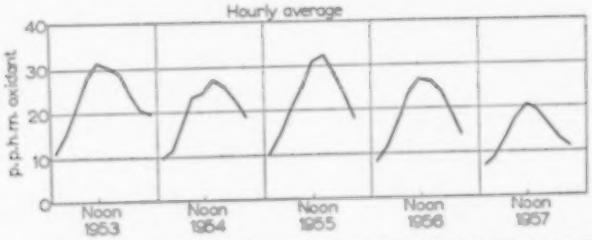

FIG. 3. Hourly average oxidant intensity vs. time of day, 1953–1957, smog months only.

at 0·5 p.p.m. the smog is generally evaluated as severe. It had also been shown that after sundown the oxidant level drops, remaining low (0·04–0·05 p.p.m.) during the night, and then rises during the daylight hours to reach a maximum at approximately noon. Fig. 3 portrays the hourly average oxidant intensity vs. the time of day for the years 1953 through 1957. This graph is based on the average of 8 months only (March through October) which might be considered the smog months.

Fig. 4 shows the daily oxidant maximum obtained from the middle of 1953 through December 1957. Values above 50 p.p.h.m. are shown in black, since they represent periods of severe smog. It can be seen that the smog intensity varies in an irregular pattern dependent to a large extent upon meteorological conditions. In general, it can be anticipated that more severe smog periods may occur in the early fall when an inversion condition frequently exists. The inversion condition coincides with very low wind velocities and very little movement of the air masses; hence, a build-up of air pollution occurs more readily at this time. On the other hand, when turbulent winds prevail, as is frequently the case during winter rain storms, no stagnation occurs and any pollutants emitted to the air are readily dispersed. This condition is reflected in the low oxidant values shown for the periods of November through February.

Two graphs are included to show the oxidant concentration vs. the day of the week. Fig. 5 indicates the number of days on which oxidant values of 50 p.p.h.m., or

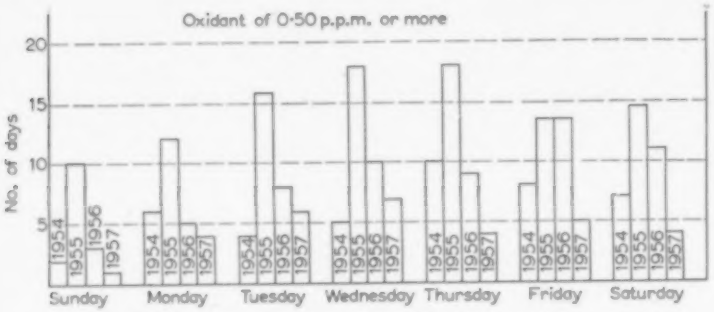

FIG. 5. Oxidant concentration vs. day of week, 50 p.p.h.m. or greater.

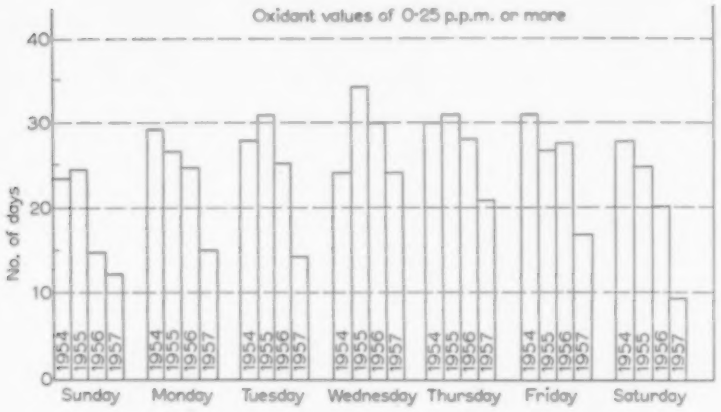

FIG. 6. Oxidant concentration vs. day of week, 25 p.p.h.m. or greater.

greater, were obtained. In Fig. 6 the number of days on which oxidant values greater than 25 p.p.h.m. were measured are shown. In general, Sunday is the day of lowest oxidant values, and the concentrations tend to rise toward Thursday and decrease somewhat toward the end of the week. This phenomenon is related to human activities, particularly to the heavy downtown traffic during the week, and to industrial emissions which are curtailed on Sunday.

Fig. 7 indicates the number of days on which the oxidant measured more than 25 p.p.h.m. vs. the month of the year. From this graph it can be seen that July, August and September have been our worst months, while in November and December there are frequently no days on which the oxidant reaches 25 p.p.h.m.

Because the irritating or nuisance effects of the smog are often a function of its intensity, as well as of its duration, the actual duration of smog in Pasadena has been plotted for the years 1953 through 1957 (see Fig. 7). A steady decrease in the duration of smog from 1953 through 1957 is shown. That this should occur in spite of the growing population, the increased number of automobiles, and the increase in fuel consumption, indicates the effectiveness of the air pollution control measures.

VOL.
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958/9

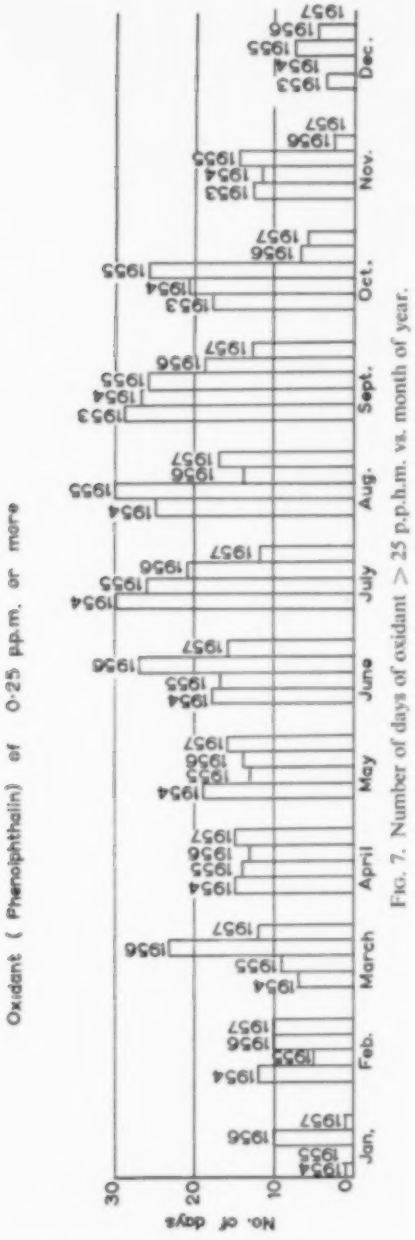

FIG. 7. Number of days of oxidant > 25 p.p.h.m. vs. month of year.

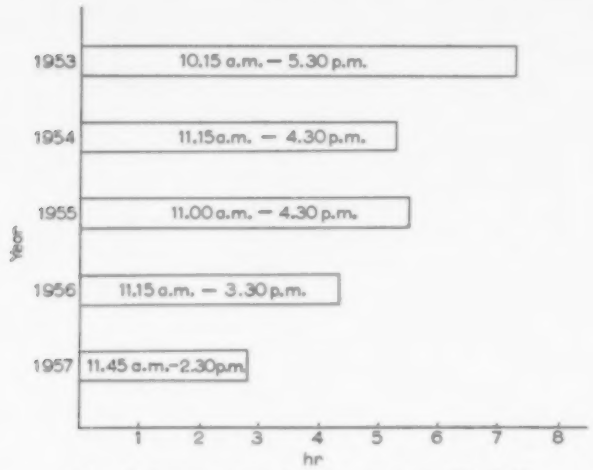

FIG. 8. Average smog duration vs. year, 1953–1957.

SUMMARY

We have found the phenolphthalin method most useful in detecting the occurrence of Los Angeles smog, and in evaluating its intensity and duration. Since the method is simple and quite inexpensive, it can be easily adapted to air pollution studies in preliminary surveys, or under circumstances where the funds required for more elaborate instrumentation are not available. Comparative measurements have been made by the State of California Department of Public Health, using the phenolphthalin method in its preliminary survey of air pollution in the San Francisco area (State of Calif., Dept. of Public Health, 1958). The method was also used by Truesdail Laboratories in a survey of air pollution in the City of Honolulu (CHARLEY and NEKOMOTO, 1958). In these cases good correlation was reported between the phenolphthalin oxidant concentration and subjective observations, and the method was considered to be most satisfactory.

VOL.
1
958/9

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A STUDY OF THE AVERAGE DISTRIBUTION OF POLLUTION AROUND STAYTHORPE

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(*Received* 28 *October* 1957)

Abstract—An examination has been made of the average distribution of sulphur pollution around Staythorpe power station in relation to sulphur output and wind statistics during the period November, 1951 to September, 1954.

Basic data, consisting of the seasonal averages of sulphur pollution as measured at fourteen observing sites at various distances and in different directions from the power station, were available as a result of a survey instigated by the Atmospheric Pollution Research Committee.

If the measurements obtained at each observing site depend on the output of sulphur dioxide from the power station, then they should also reflect the wind distribution in the area. The importance of wind direction is self-evident, but wind speed must also be taken into account since, for a constant distance from an elevated source, concentrations are inversely proportional to wind speed. The fact that the individual observing sites were at varying distances from the power station was another factor that had to be considered. This is so because the ground level concentration downwind of an elevated source is small near the source, increases to a maximum some distance away and then falls off steadily as one moves still further from the source. This important factor was dealt with by studying the pattern of pollution in the area and then estimating concentrations along arcs of a circle of specified radius about the power station.

The data for winter and summer half-years separately are shown to support a relation, which follows from conventional treatment of diffusion from a point source, of the form

$$p = a + b\frac{f(\theta)\,S}{\bar{u}}.$$

In this relation p is the observed pollution for the half-year, at a distance of 1500 yd and averaged over an octant about the power station, $f(\theta)$ is the percentage frequency of occurrence of wind directions in the corresponding octant, $\bar{u}$ is the corresponding mean wind speed, and S is the average monthly output of sulphur dioxide during the half-year.

The quantity a, logically a "background" pollution, has values which are close to the winter and summer pollution existing immediately before the power station was commissioned. The magnitude of the coefficient b is shown to be consistent with previous ideas and other recent data on the vertical diffusion from an elevated point source.

1. INTRODUCTION

OVER a number of years surveys of sulphur dioxide pollution around power stations have been carried out by the Central Electricity Authority and by the Fuel Research Station of the Department of Scientific and Industrial Research. Analysis of the observational data thus obtained had hitherto generally failed to reveal any significant correlation between the amount of coal consumed at a station and the average sulphur dioxide pollution as measured at a number of sites surrounding the station. It has proved difficult to account for this absence of correlation, and a number of possibilities, mainly concerned with variations in meteorological conditions from one period to another, have been suggested.

With the object of studying in more detail the meteorological effects involved and at the invitation of the Atmospheric Pollution Research Committee, the authors

VOL 1 1958

have examined the reports of pollution surveys around a number of power stations. The analysis of observations described in these reports consisted mainly of a direct comparison between coal consumption or sulphur dioxide output and the average values of the pollution measured at all the observing sites around each power station. It appeared, however, that such a procedure was not sufficiently detailed to permit any correlation, if one existed, to emerge.

It was decided, therefore, to examine the observations of sulphur dioxide pollution as measured at the individual sites around a power station. In this manner the pattern of pollution instead of its overall average became the main subject of investigation and the objective was to ascertain whether this pattern could be explained in terms of the total sulphur dioxide output and the local distribution of wind speed and wind direction. An investigation on these lines concerned with one power station, that at Staythorpe in Nottinghamshire, is described in the present paper. Staythorpe is a country district, remote from such complicating factors as built-up areas and industrial plants, and its power station was therefore considered the most appropriate for a first or pilot investigation of this kind. Observations made before the power station was commissioned had shown a uniform distribution of sulphur dioxide pollution in the area. In the following sections the results obtained from an analysis of the Staythorpe data for the three winters and three summers from November, 1951 to September, 1954 are described.

2. DATA AVAILABLE

In the absence of wind records for Staythorpe itself, those for the nearest meteorological station, Swinderby, were used. Staythorpe lies about 10 miles to the south-west of Swinderby and it seems highly probable that the wind conditions at the two places are closely similar.

Fig. 1 shows the average SO_2 pollution around Staythorpe for each season from the summer of 1948 to the summer of 1954 and also the total coal consumption each season from the time of commissioning the power station in the summer of 1950. Thus the data in this figure, although going back well beyond the period with which the present investigation is concerned, show usefully the seasonal trend in average SO_2 pollution both before and after the power station came into operation. It will be noted from Fig. 1 that each season consists of 5 months, the summer extending from May to September and the winter from November to March.

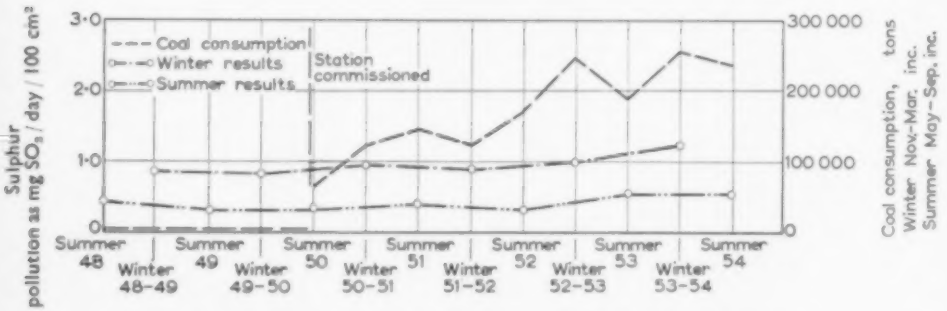

FIG. 1. Staythorpe. Seasonal coal consumption and pollution averages.

Table 1, which is supplementary to Fig. 1, gives for each season the coal consumption and sulphur dioxide emission expressed in thousands of tons/month and in tons/month respectively.

TABLE 1. FUEL CONSUMPTION AND SULPHUR DIOXIDE EMISSION—STAYTHORPE

Season	Fuel consumed (thousand tons/month)	SO_2 emission (tons/month)
Winter 1951–52	25·2	273
Summer 1952	34·0	536
Winter 1952–53	49·9	881
Summer 1953	38·2	706
Winter 1953–54	51·6	1050
Summer 1954	55·3	1210

At Staythorpe concentrations of sulphur dioxide in the air are measured (MEETHAM, 1956) by the " lead peroxide " method. A glass or porcelain cylinder is coated with lead peroxide paste and exposed in a louvered box which ensures protection from rain while permitting the free access of air. The paste absorbs sulphur dioxide from the air to form lead sulphate. After exposure for one calendar month the cylinder is removed and analysis of the paste then gives the amount of sulphur dioxide absorbed. This quantity is expressed as mg SO_3 per day per 100 cm².

FIG. 2. Staythorpe. Sulphur dioxide as mg SO_3 per day per 100 cm² for winter November 1951 to March 1952.

In Fig. 2 the fourteen observing sites around the power station at Staythorpe are indicated by means of small circles. The figures within the circles are the measured concentrations (in mg SO_3 per day per 100 cm^2) for the winter period November, 1951 to March, 1952. Contours have been drawn to represent concentrations of 0·9 and 1·0 in these units. Corresponding diagrams for the other five seasons are not reproduced but estimated concentrations derived from them are given in Tables 4 and 5. In Fig. 1 the average values of pollution plotted for each season are the means of the observations recorded at all fourteen sites.

The percentage frequency of winds in each octant and the weighted mean speed for each octant for the three winters and three summers respectively at Swinderby are shown in Tables 2 and 3 below. The raw data showed for each octant the total times during which the wind speed fell within the ranges 1–3, 4–6, 7–10, etc. knots and for reasons which will appear later the mean wind speed was derived from the reciprocal of the speed in the middle of each range weighted according to the given time. After the mean speeds had been calculated, the percentage of calms in a season was distributed uniformly among the eight octants which in Tables 2 and 3 are shown in clockwise order from the north.

TABLE 2. SWINDERBY WIND DISTRIBUTION—WINTER SEASONS

Octant	Winter 1951–52		Winter 1952–53		Winter 1953–54	
	Percentage frequency	Mean speed (knots)	Percentage frequency	Mean speed (knots)	Percentage frequency	Mean speed (knots)
0–45°	4·2	5·4	10·4	7·0	6·9	6·9
45–90°	5·1	5·4	7·0	6·1	11·0	6·7
90–135°	7·4	5·4	4·1	5·1	11·2	7·6
135–180°	13·5	7·0	7·8	4·5	17·3	8·1
180–225°	21·7	9·7	24·4	7·5	26·7	9·0
225–270°	23·9	11·3	15·2	8·4	11·6	9·7
270–315°	12·7	9·5	8·1	8·3	5·8	8·8
315–360°	11·5	7·8	23·0	8·5	9·5	8·0

TABLE 3. SWINDERBY WIND DISTRIBUTION—SUMMER SEASONS

Octant	Summer 1952		Summer 1953		Summer 1954	
	Percentage frequency	Mean speed (knots)	Percentage frequency	Mean speed (knots)	Percentage frequency	Mean speed (knots)
0–45°	9·2	6·9	9·4	6·9	8·7	8·0
45–90°	6·8	5·7	6·2	5·8	2·3	4·6
90–135°	4·5	3·1	6·4	5·5	2·7	5·0
135–180°	8·2	5·3	10·6	7·3	11·0	7·2
180–225°	17·7	7·1	25·0	9·3	25·3	9·6
225–270°	24·1	9·3	21·2	9·6	22·0	10·0
270–315°	16·8	8·3	11·5	9·4	13·5	8·9
315–360°	12·7	7·1	9·7	6·6	14·5	8·3

3. ANALYSIS PROCEDURE

In the present analysis we shall be concerned with the ground-level concentration over a circle of radius x from a *point source* of strength Q units per second at height h.

If the cloud is instantaneously narrow in the lateral (crosswind) direction, a condition which will normally hold, the integrated concentration around the circle may be taken to be equal to the concentration at distance x from an *infinite crosswind line source* of strength Q units/cm sec at the same height. It then follows that the average concentration in any octant of the circle must be of the form

$$\frac{f(\theta)}{12{\cdot}5} \cdot \frac{1}{2\pi x}\, g(h, x)\, \frac{Q}{\bar{u}} \tag{1}$$

where: $\bar{u}$ = mean wind speed assumed constant with height.

$f(\theta)$ = percentage frequency of wind directions in the corresponding octant.

$g(h, x)$ = function of the vertical shape and size of the cloud. If, for example, the vertical distribution is Gaussian with standard deviation σ, the wind velocity is constant with height and the cloud is simply reflected from the ground.

$$g(h, x) = \frac{2}{\sqrt{(2\pi)}\sigma} \exp\left(\frac{-h^2}{2\sigma^2}\right) \tag{2}$$

(This expression follows immediately from a crosswind integration of the point source formula deduced by SUTTON (1947, equation (6), p. 429) and the substitution of the form

$$\sigma^2 = \tfrac{1}{2}C_z^2\, x^{2-n}.)$$

The pollution at Staythorpe will also include a " background " contribution, a, due to distant sources. This quantity may vary from one summer to another or from one winter to another since the wind distribution in any season does not conform exactly to the average. In the case of Staythorpe, however, the sulphur dioxide pollution before the power station came into operation was found to be uniformly distributed with practically constant summer and winter values (Fig. 1). It therefore seemed reasonable to regard the quantity a as constant for the purposes of our analysis. The total average value of the concentration p over any octant may then be written

$$p = a + b\,\frac{f(\theta)S}{\bar{u}} \tag{3}$$

where, if p and a are in units* of mg SO_3 per day per 100 cm², S is the number of tons of sulphur dioxide discharged per month in a particular season, and if $\bar{u}$ and x are expressed in knots and yards respectively,

$$b = \frac{8{\cdot}511 \times 10^8\, g(h, x)}{x} \tag{4}$$

In equation (4), $g(h, x)$ is still in c.g.s. units.

The extent to which the relation (3) is supported by the data is examined below, firstly with regard to the functional form and secondly with regard to the absolute magnitude of the quantity $g(h, x)$.

We proceeded in the following manner:

(a) A circle was drawn around the power station on each pollution diagram (Fig. 2) to represent a distance of 1500 yd from the station. Radial lines

* For the conversion involved here a relation was supplied by the Fuel Research Station in the form : " concentration in parts per 100 million of sulphur dioxide = 4·2 × pollution in mg SO_3 per day per 100 cm² ".

were also drawn in order to indicate the octants and to divide the circle into eight equal arcs.

(b) The quantity $f(\theta)S/\bar{u}$ in respect of each octant was calculated for the three winters and three summers, an allowance being made for the percentage of calms that occurred in each season.

(c) From each pollution diagram the actual seasonal concentration in each octant at a distance of 1500 yd from the power station was estimated. At this distance it was thought that the pollution level would not be sensitive to any local effect such as that evident at the site nearest the power station itself, i.e. at the centre of the large circle in Fig. 2. This observing site was noteworthy for comparatively high concentrations which could not readily be explained by the general background pollution and the output from the chimney.

Taking the seasons separately, the data formed twenty-four pairs of values of the quantity $f(\theta)S/\bar{u}$ and of the corresponding estimated actual concentration, the latter representing p on the left-hand side of equation (3). The next stage was therefore to ascertain whether there existed between the two parameters a functional relationship of the form shown in this equation. This part of the investigation is described in the following two sections.

4. WINTER POLLUTION

The values of p and $f(\theta)S/\bar{u}$ that were tested for relationship are given in the following Table 4.

TABLE 4

Octant	1951–52		1952–53		1953–54	
	$f(\theta)S/\bar{u}$	p	$f(\theta)S/\bar{u}$	p	$f(\theta)S/\bar{u}$	p
0–45°	$2{\cdot}12 \times 10^2$	0·80	$13{\cdot}09 \times 10^2$	0·97	$10{\cdot}50 \times 10^2$	1·00
45–90°	$2{\cdot}58 \times 10^2$	0·76	$10{\cdot}11 \times 10^2$	0·97	$17{\cdot}24 \times 10^2$	0·92
90–135°	$3{\cdot}74 \times 10^2$	0·94	$7{\cdot}08 \times 10^2$	0·98	$15{\cdot}47 \times 10^2$	1·10
135–180°	$5{\cdot}27 \times 10^2$	0·89	$15{\cdot}27 \times 10^2$	1·04	$22{\cdot}43 \times 10^2$	1·28
180–225°	$6{\cdot}11 \times 10^2$	0·95	$28{\cdot}66 \times 10^2$	1·12	$31{\cdot}16 \times 10^2$	1·35
225–270°	$5{\cdot}77 \times 10^2$	0·97	$15{\cdot}94 \times 10^2$	1·10	$12{\cdot}56 \times 10^2$	1·32
270–315°	$3{\cdot}65 \times 10^2$	0·96	$8{\cdot}60 \times 10^2$	1·00	$6{\cdot}92 \times 10^2$	1·29
315–360°	$4{\cdot}03 \times 10^2$	0·88	$23{\cdot}84 \times 10^2$	0·94	$12{\cdot}47 \times 10^2$	1·10

Note: The values of p (observed concentration) have been rotated through 180° in order to correspond with the wind distribution.

By the method of least squares the best straight line to fit these pairs of values of p and $f(\theta)S/\bar{u}$ was found to be:

$$p = 0{\cdot}89 + 1{\cdot}16 \times 10^{-4} \frac{f(\theta)S}{\bar{u}} \qquad (5)$$

The closeness of fit may be judged from Fig. 3 in which are shown the straight line given by the above equation together with a plot of all the points listed in Table 3. It will be seen that for most of the points the straight line provides a good representa-

tion. However, it seemed desirable to apply some quantitative criterion in order to estimate the extent to which the straight line does adequately represent the observations.

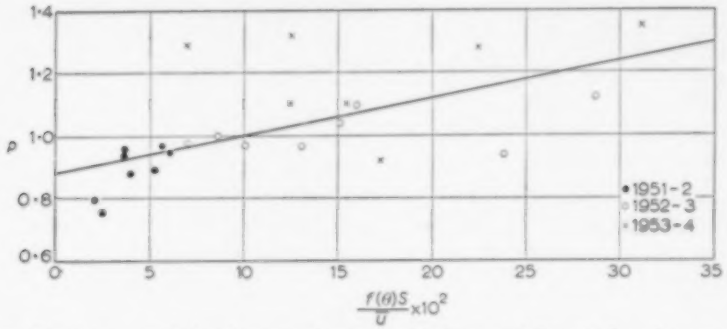

FIG. 3. Staythorpe. Relation between observed pollution p and $f(\theta)\,S/\bar{u}$ for winter seasons.

The most suitable index is the correlation coefficient, R, between the observed values of p and the corresponding values computed from equation (5) above. The value of R is given by

$$R = 1 - \Sigma\epsilon^2/\Sigma p_d^2$$

where ϵ = observed p − calculated p
p_d = observed $p - \bar{p}$
$\bar{p}$ = mean value of observed p's

Applied to the above observations and the straight line, the value of R was found to be 0·604. In the *Handbook of Statistical Methods of Meteorology*, BROOKS and CARRUTHERS give, for the conditions of this problem, a value 0·404 for the 5 per cent point of R and a value 0·515 for the 1 per cent point of R.

The computed value of R, i.e. 0·604, is considerably better than the 1 per cent point and for the winter season, therefore, we may attribute some significance to the relationship,

$$p = 0{\cdot}89 + 1{\cdot}16 \times 10^{-4}\,\frac{f(\theta)S}{\bar{u}}$$

between the observed pollution at Staythorpe and a quantity based on the wind distribution and the output of sulphur dioxide at the power station.

A feature of this result is worthy of special comment. The value of the constant term (0·89) can be seen by reference to Fig. 1 to approximate closely to the average pollution which existed before the power station was commissioned, i.e. when S in the above equation was zero. The fact that this constant term is so nearly equal to the original background pollution lends support to the significance of the equation.

5. SUMMER POLLUTION

For the summer seasons, the values of p and $f(\theta)S/\bar{u}$ that were tested for relationship are given in Table 5.

TABLE 5

Octant	1952		1953		1954	
	$f(\theta)S/\bar{u}$	p	$f(\theta)S/\bar{u}$	p	$f(\theta)S/\bar{u}$	p
0–45°	$7{\cdot}15 \times 10^2$	0·27	$9{\cdot}62 \times 10^2$	0·42	$13{\cdot}16 \times 10^2$	0·58
45–90°	$6{\cdot}39 \times 10^2$	0·26	$7{\cdot}54 \times 10^2$	0·36	$6{\cdot}05 \times 10^2$	0·44
90–135°	$7{\cdot}78 \times 10^2$	0·37	$8{\cdot}21 \times 10^2$	0·47	$6{\cdot}53 \times 10^2$	0·46
135–180°	$8{\cdot}29 \times 10^2$	0·35	$10{\cdot}25 \times 10^2$	0·54	$18{\cdot}49 \times 10^2$	0·44
180–225°	$13{\cdot}37 \times 10^2$	0·42	$18{\cdot}98 \times 10^2$	0·72	$31{\cdot}88 \times 10^2$	0·78
225–270°	$13{\cdot}89 \times 10^2$	0·40	$15{\cdot}59 \times 10^2$	0·67	$26{\cdot}62 \times 10^2$	0·74
270–315°	$10{\cdot}85 \times 10^2$	0·34	$8{\cdot}64 \times 10^2$	0·56	$18{\cdot}35 \times 10^2$	0·63
315–360°	$9{\cdot}59 \times 10^2$	0·28	$10{\cdot}38 \times 10^2$	0·50	$21{\cdot}13 \times 10^2$	0·64

Note: The values of p (observed concentration) have been rotated through 180° in order to correspond with the wind distribution.

As for the winter data, the method of least squares was again used and gave the following straight line equation:

$$p = 0{\cdot}26 + 1{\cdot}78 \times 10^{-4} \frac{f(\theta)S}{\bar{u}}. \tag{6}$$

This line is shown in Fig. 4 where the points of Table 5 are also plotted and can be seen to conform reasonably well with the straight line.

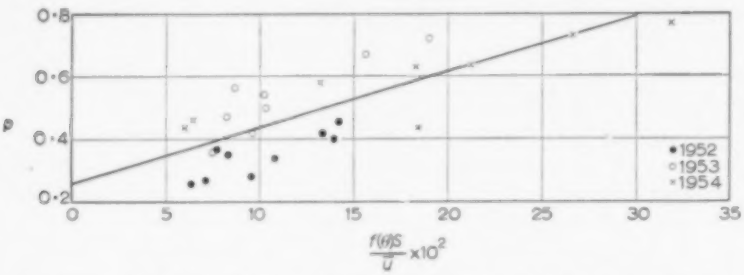

FIG. 4. Staythorpe. Relation between observed pollution p and $f(\theta)\,S/\bar{u}$ for summer seasons.

The correlation coefficient R, computed in the manner described in the preceding section, was found to be 0·804, i.e. a value considerably better than the 1 per cent point of R (0·515) and therefore significant. The constant term (0·26) can be seen from Fig. 1 to be approximately equal to the summer background pollution before the power station began to function, a result which corresponds with that found in the winter analysis.

6. THE MAGNITUDE OF $g(h, x)$ AND ASSOCIATED DIFFUSION PARAMETERS

Our analysis has so far been confined to the functional form of the relationship between pollution and the conditions of output and wind distribution. We now seek to extend the analysis in a more explicit way, by examining the absolute values of the coefficient b in equation (3). From equations (2), (3) and (4) and from the values of b contained in equations (5) and (6), we may derive values of σ, the " standard deviation " of the vertical distribution which the cloud must possess (apart from the

effect of the boundary) in order to explain the observed pollution at ground level.

We need first to assign a value to h, the effective height of the source. This is equal to the height of the chimney added to the vertical distance by which the discharged gases are raised in consequence of their initial buoyancy and upward velocity. Several formulae are available for calculating the effective height in problems of this nature and we selected the Oakridge formula which is simple to apply and which was recommended by the COMMITTEE ON AIR POLLUTION (1954). This formula is:

$$uz = 1{\cdot}5vd + 0{\cdot}4Q_H \text{ (c.g.s. units)}$$

where u is the wind velocity, v is the velocity of efflux of the gases, d is the chimney diameter, Q_H is the heat output in cal/sec, z is the height reached by the gases measured from the mouth of the chimney, so the effective height h is equal to z plus the chimney height.

If the air temperature is T_1°A and the gases are discharged at a temperature $(T_1 + \Delta)$°A, then assuming the gases have the same specific heat C_p and, at T_1°A, the same density as the air,

$$Q_H = \frac{\pi}{4} d^2 v \left(\frac{T_1}{T_1 + \Delta} \right) \rho C_p \Delta$$

hence

$$uz = Q_H \left\{ 0{\cdot}4 + \frac{6}{\pi} \frac{(T_1 + \Delta)}{T_1 \rho C_p \Delta d} \right\}$$

For Staythorpe $T_1 + \Delta = 419$°A, the chimney diameter is 20 ft and Q_H is obtained from the coal consumption, each pound of coal burnt yielding 153 ft³ of gas at s.t.p. With these data combined with mean wind velocities for each season, an average effective height for the six seasons was derived. The value obtained for h was 504 ft and this was approximated to 500 ft for further calculations on the magnitude of $g(h, x)$ and thence of σ.

Comparisons between equations (3), (4) and (5) and between equations (3), (4) and (6) permit the following values to be derived for $g(h, x)$, for $h = 500$ ft and $x = 1500$ yd:

$$\text{Winter } g(h, x) = 2{\cdot}05 \times 10^{-5} \text{ cm}^{-1}$$
$$\text{Summer } g(h, x) = 3{\cdot}14 \times 10^{-5} \text{ cm}^{-1}$$

From Fig. 5, a graph showing the variation of g with σ for $h = 500$ ft, the values of σ corresponding to these values $g(h, x)$ can be determined and are seen to be:

$$\text{Winter } \sigma = 90 \text{ or } 390 \text{ yd}$$
$$\text{Summer } \sigma = 150 \text{ or } 180 \text{ yd}$$

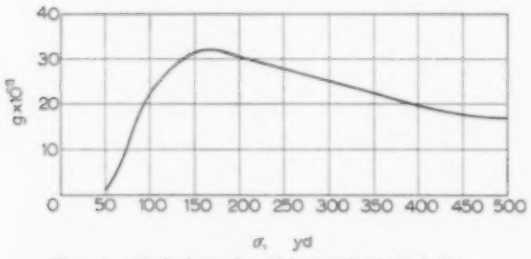

FIG. 5. Variation of g with standard deviation.

It is common experience that the vertical component of turbulence is greater in the summer than in the winter months and as a general rule we should therefore expect the summer value of σ to be greater than the winter value. We therefore reject the value of 390 yd for winter and conclude that the true values of σ are approximately 90 yd for the winter and between 150 and 180 yd for the summer.

The results for σ refer to a distance of 1500 yd from the source and can be converted approximately to an angular deviation given by $\tan^{-1}\sigma/1500$. The values obtained are 3·5° for the winter and between 5·7° and 6·8° for the summer months. These figures appear reasonable as regards order of magnitude and can be compared with some results recently obtained by HAY and PASQUILL (1956) and reported to the Meteorological Research Committee. Their experiments, which were conducted at Porton in the early autumn included the measurement of the vertical distribution of airborne particles released mainly at a height of 500 ft and sampled at downwind distances up to 500 m. The results indicated that the vertical spread of the cloud of particles varied approximately linearly with the distance of travel, and the corresponding standard (angular) deviations fell in the range 1·7° to 6·0°. These values are very similar to those derived above from the Staythorpe data.

Another parameter which can be evaluated is the vertical diffusion coefficient, C_z, which occurs in SUTTON's treatment of diffusion and is given by

$$C_z = \sigma\left(\frac{2}{x^{2-n}}\right)^{1/2}$$

Taking $n = 0{\cdot}25$, $x = 1500$ yd and the winter and summer values of σ in turn and working in c.g.s. units, we find:

Winter $C_z = 0{\cdot}37$ cm$^{1/8}$ $= 0{\cdot}21$ m$^{1/8}$
Summer $C_z = 0{\cdot}49$ to $0{\cdot}75$ cm$^{1/8}$ $= 0{\cdot}35$ to $0{\cdot}42$ m$^{1/8}$

These values for C_z may be compared with those obtained by STEWART *et al.* (1954) from measurements of the diffusion of the gases discharged from the Harwell Pile. For distances up to 800 m they found the following mean values of C_z

Inversion conditions 0·11 m$^{1/8}$
Adiabatic conditions 0·20 m$^{1/8}$
Lapse conditions 0·25 m$^{1/8}$

At greater distances, up to 1050 m, STEWART *et al.* report values of 0·32 m$^{1/8}$ for C_z in lapse and adiabatic conditions.

The present results are thus obviously consistent with two independent experimental studies of the vertical diffusion from an elevated source. Moreover, it might even be argued that the rather greater degree of vertical diffusion implied by the present results is in keeping with the fact that they represent an average over several months whereas the results with which they are compared represent averages over the order of 1 hr. On the other hand it should be remembered that the treatment applied here is only approximate, especially in the sense that the influence of the variation of output and wind speed on the effective height of the source are neglected. The detailed agreement obtained is therefore to be regarded as fortuitous to some extent.

7. CONCLUDING DISCUSSION

It has been shown that for the three winter and three summer seasons that have formed the period of this investigation, the distribution of sulphur dioxide pollution

VOL. 1 58/9

around Staythorpe was significantly related to a parameter incorporating in a simple fashion the sulphur emission at the power station and the distribution of wind speed and direction near the site. In addition, the relationship found has provided values of diffusion parameters which compare reasonably with the values obtained experimentally by other workers.

In the present analysis we have not attempted to examine the separate effects of output and wind conditions. However, from an inspection of Figs. 3 and 4, bearing in mind the variation in output from year to year (Table 1) it is fairly evident that the relation between p and $f(\theta)/\bar{u}$ alone would be less systematic than that between p and $f(\theta)S/\bar{u}$.

This investigation, which has been based on a detailed study of the pattern of pollution around a power station, has led to conclusions which could not have been drawn from a consideration of the average pollution in the area. Our results therefore suggest that the average pollution, which is commonly used in studies of this kind and is in fact the unweighted mean of readings taken at various distances from a power station, may prove misleading both for year by year comparisons at one power station and for comparisons between different power stations. Consideration might well be given to devising a system of weighting the individual observations in accordance with the wind distribution and the distance from the source before local averages are worked out.

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THE ATMOSPHERIC POLLUTION OF CITIES

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Abstract—The paper assesses the pollution levels of sulphur dioxide (and smoke) likely to be produced by the thousands of domestic fires in large cities. It shows that the major part of the pollution measured in large cities can be attributed to domestic fires even though the concentrations produced by a single fire are negligible.

An approximate formula is given so that city concentrations can be estimated if the rate of emission, the wind speed, and the size of the city are specified.

The worst pollution occurs about a mile downwind of the centre of the city and pollution levels decrease extremely rapidly outside the city boundary, particularly when averaged over a range of wind directions. When the atmosphere is stable, ground-level concentrations tend to be high. The effect of fog is complex and uncertain. It appears likely, however, that SO_2 (and smoke) is removed by the fog and that the " time constant " is between 8 and 20 hr.

INTRODUCTION

ALTHOUGH the pollution of cities has been measured for many years and abominated even longer, it is not possible even today to allocate responsibility for the results obtained by any particular sulphur candle in any British city to a particular source or type of source. There are mathematical methods for assessing the sulphur dioxide concentrations produced by large sources with high chimneys (HAWKINS and NONHEBEL, 1955) and although these may not be perfect they undoubtedly allow the seriousness of pollution by large sources to be assessed. No such methods have been used for manifold small sources.

However, there has been growing awareness of the contribution of domestic fires to the pollution of cities and it is highly desirable that a quantitative assessment should be made so that comparisons can be made with other classes of pollution source. The present paper is an attempt to put the pollution effect of large numbers of domestic fires on a quantitative basis. The treatment is applied to the case of sulphur dioxide but the implications with suitable adjustments would be similar in the case of smoke.

THE BASIS OF CALCULATION

It is known that the plume from a simple source diverges as it proceeds downwind due to diffusion processes. If the diffusion were due to processes which were small compared with the width of the plume the outline of the plume would be a parabola, i.e. the width would be proportional to $x^{\frac{1}{2}}$ where x is the distance from the source. (This does not apply near the source where it would require the source to be infinitely small with infinite concentration.) It is sometimes suggested that a plume is a cone, i.e. that the width is proportional to x. It would be difficult to support this by any diffusion theory but it does represent a very simple approach to the plume and also the limit to conceivable values for the index of x. SUTTON (1947) has considered the fact that the diffusion processes have a range of magnitudes compared with the width of the plume and has deduced formulae where the index of x is between the values $\frac{1}{2}$ and 1 varying according to atmospheric conditions. He has assumed

that, in cross-section, the concentration of pollutant in a plume is represented by the well-known error function, and, having allowed for source height and the effect of the ground, has produced the formula :

$$C=\frac{W\exp\{-y^2/C_y^2x^{2-n}\}}{\pi C_yC_zUx^{2-n}}\left[\exp\left\{-\frac{(z-h^2)}{(C_z^2x^{2-n})}\right\}+\exp\left\{-\frac{(z+h)^2}{(C_z^2x^{2-n})}\right\}\right]$$

where C is the concentration

W is the rate of emission of pollutant

h is the height of emission above ground level

U is the wind speed

C_y, C_z, and n are meteorological constants.

The concentration at ground level is obtained by putting $z=0$ and is

$$C_0=\frac{2W}{\pi C_yC_zUx^{2-n}}\left\{\exp\left(\frac{-h^2}{C_z^2x^{2-n}}\right)\right\}\exp\left(\frac{-y^2}{C_y^2x^{2-n}}\right)$$

The concentration at height h is given by putting $z=h$ and is

$$C_h=\frac{W}{\pi C_yC_zUx^{2-n}}\left\{1+\exp\left(\frac{-4h^2}{C_z^2x^{2-n}}\right)\right\}\exp\left(\frac{-y^2}{C_y^2x^{2-n}}\right).$$

In order to apply these formulae to a city it will be assumed that the sulphur dioxide emitted by domestic fires is emitted uniformly from the whole surface of the city instead of being emitted from many point sources. As a result, the effects very close to individual chimneys will not be truly represented but the overall effect of the town can be calculated.

Let the average emission of pollutant per unit area be w. Substituting $w\,dx\,dy$ for W, SUTTON's equation represents the effect of each of the infinitesimal sources which contribute to the pollution of the city.

The concentration at ground level at a point which is a distance x from the windward edge of a town is given by

$$C_0=\int_0^x\int_{y_2}^{y_1}\frac{2w\exp(-h^2/C_z^2x^{2-n}-y^2/C_y^2x^{2-n})}{\pi C_yC_zUx^{2-n}}\,dx\,dy.$$

Provided the width of the city represented by y_1 and y_2 is not small compared with x there is no appreciable error in replacing y_1 and y_2 by $+\infty$ and $-\infty$. We then have after integration

$$C_0=\frac{2w}{\sqrt{\pi}C_zU}\int_0^x\frac{\exp(-h^2/C_z^2x^{2-n})}{x^{1-n/2}}\,dx. \tag{1}$$

The corresponding concentration at height h is

$$C_h=\frac{W}{\sqrt{\pi}C_zU}\int_0^x\frac{1+\exp(-4h^2/C_z^2x^{2-n})}{x^{1-n/2}}\,dx. \tag{2}$$

In order to evaluate these expressions values must be assigned to the various constants. These values are of course arguable but representative values which are thought to be the best available at present have been assessed as follows.

The height of the domestic chimney is assumed to be 30 ft but its effective height will vary with wind speed. It has been observed that under normal conditions the plume rise is negligible with a wind speed of 5 ft/sec and is about 5 ft with a wind speed of 3 ft/sec. As a rough approximation the plume rise is assumed to be $5\times(3/U)^3$ ft where U is the wind speed in ft/sec. (This formula is based on the plume rise formula due to SUTTON (1950).) The same law is assumed to apply under stable* conditions except that with very low wind speeds it is limited. Under completely calm

* There is some ambiguity about the use of the word " inversion ". Throughout the paper the phrase " stable conditions " has been used to indicate that the potential temperature of the atmosphere increases with height. The phrase " neutral conditions " indicates that the potential temperature is constant with increasing height.

VO 1 1958

conditions with an inversionary lapse rate of potential temperature of 2×10^{-4}° C/cm it has been calculated by PRIESTLEY and BALL (1955) that the plume from a heat source equivalent to a domestic chimney will rise 50 ft above its source. During the calculations it has therefore been assumed that under stable conditions the plume effective height is as shown in Table 1.

TABLE 1

Wind speed (ft/sec)	0	½	1	2	3	5	>5
Effective height of chimney (ft) (Stable conditions)	80	80	80	45	35	30	30

TABLE 2

	n	C_z^2
Zero or small temperature gradient, " neutral " conditions	¼	0·007 ft^n
Large inversion (very stable)	½	0·00225 ft^n

The total emission of sulphur dioxide has been calculated by using the figure given in the Beaver Report, that the total emission of sulphur dioxide from domestic sources is $0{\cdot}9 \times 10^6$ tons/annum (or 350 ft³/sec). This is assumed to be the amount emitted by the fires of 50 million people. The density of population in Greater London, with a diameter of approximately 40 miles, is one person to 2500 ft² (*Reference Atlas of Greater London*). (In the L.C.C. area the population density is two and a half times as high.) Combining these figures, one obtains a figure for the emission of sulphur dioxide of $3{\cdot}6 \times 10^{-9}$ ft³/ft² sec for the area of Greater London. This is the figure for the average annual rate. If we assume a factor of 2, because nearly all the coal is burnt in the six winter months, a factor of 1·6, because most of the coal is burnt by day, and a factor of 1·5 for cold weather conditions (32°F compared with 42°F), i.e. that 50 per cent more coal is burned on cold days than the average, we obtain a figure of $1{\cdot}7 \times 10^{-8}$ ft³/ft² sec for the rate of emission of sulphur dioxide in cold weather. The meteorological constants are those given by SUTTON and quoted by BRYANT and COWDREY (1955) and are shown in Table 2.

Using these values, the expressions (1) and (2) have been evaluated by laborious numerical integration, for a range of wind speeds and for both neutral and stable conditions. The evaluations have not been made for superadiabatic conditions since these are not usually associated with severe pollution and since the effects obtained are approximately similar but opposite to the effects produced by stable conditions.

The integrations carried out are not convenient and cannot be easily manipulated. For the sake of experiment, SUTTON's formulae have therefore been modified on the assumption that a plume is in the form of a cone. The semi-angle is assumed to be 5° for neutral conditions and 1·5° for stable conditions. The width of the plume in each case agrees with the width given by SUTTON's formula at a distance of about 300 ft from the source and to that extent both agree with the commonly observed appearance of plumes.

Equation (1) becomes

$$C_x = \frac{W}{\sqrt{\pi} C_z U} \left\{ \ln \frac{C_z^2 x^2}{h^2} + \frac{h^2}{C_z^2 x^2} - \frac{h^4}{C_z^4 x^4 \times 2 \times 2!} + \frac{h^6}{C_z^6 x^6 \times 3 \times 3!} \cdots \right\} \qquad (3)$$

where $C = 0{\cdot}041$ for normal conditions and $C = 0{\cdot}0114$ for stable conditions. This is referred to as the " cone " formula.

The results obtained for neutral conditions (but not for stable conditions) are not very different from those obtained using SUTTON's formula. It is therefore possible to say that, to a good approximation, equation (3) gives the ground-level concentration due to an area source such as a town, under neutral conditions and the use of this equation is much simpler than numerical integration. For example, using this formula it is convenient to evaluate the concentrations which obtain in the lee of a city. If a city has a diameter l, the concentration at a distance X ($X > l$) along the wind direction through the city centre $= C_x - C_{x-l}$.

This formula only applies while the city is effectively an infinite crosswind source. When $X > 6l$

fresh air from the sides of the pall begins to affect the concentration in the middle and the concentration then falls off more rapidly than the formula indicates.

RESULTS OBTAINED

Fig. 1 shows the concentrations in p.p.m. by volume of SO_2 obtained at ground level and at effective chimney height for different wind speeds plotted against distance under stable conditions.*

(The effective plume height is different for the different wind speeds.)

Fig. 2 shows the concentrations obtained at ground level and at effective plume height under conditions of neutral atmospheric lapse rate.

In both figures the results obtained by " cone " formula are shown dotted.

Fig. 3 shows the variation of concentration with wind speed plotted at four different distances from the windward side of the town. For wind speeds above 5 ft/sec the variations of plume height are negligible and the concentration is inversely proportional to wind speed.

Fig. 4 shows the result obtained when the stable layer is assumed to have only a limited depth, in this case 100 ft. This only has an important effect on the concentrations obtained when the effective plume height becomes comparable with the height of the stable layer and so has not been calculated for greater thicknesses of stable layer, since in these cases the results would be almost identical with the results previously obtained where the stable layer is assumed to have unlimited height.

SUTTON's formula was applied to the case of a stable layer of limited height by assuming that, just as the effect of the ground could be simulated by a positive image source below ground level, the effect of the top of the stable layer could be simulated by a negative image source reflected in the top of the stable layer. This is equivalent to assuming that any gas which penetrates the stable layer is immediately and completely removed. In principle it is also necessary to consider the negative image of the ground image reflected in the top of the stable layer and so on. In practice this adds little to the calculation.

It must be pointed out that the patterns shown in Figs. 1–4 are equilibrium patterns and take a greater or less time to develop according to the distance and wind speed considered. For example, the concentration at 100,000 ft for 1 ft/sec wind speed would require both the emission rate and the stable conditions to persist for 28 hr.

Emission during night is very much less than during the day. Fig. 5 shows the results obtained under stable conditions by assuming that emission continues for 15 hr out of 24 but is zero for the remaining 9 hr.

Fig. 6 shows the pattern of pollution in the lee of a city (a) 30,000 ft across (b) 150,000 ft across. Fig. 6 (c) shows the mean concentration at places outside the city 150,000 ft across, allowing for the fact that the wind does not blow from a fixed direction.

DISCUSSION OF RESULTS

Fig. 1 very clearly illustrates how the concentration of sulphur dioxide from the multitude of tiny sources builds up. It indicates that the highest concentrations are to be expected at some height above the ground. It might be thought that the concentration at plume height should tend to the same value as the concentration at ground level at large distances. This is not the case because even at large distances

* The Beaver Report states that the weight of domestic smoke emitted is equal to the weight of domestic SO_2 emitted. The results obtained can therefore be applied to smoke, if 1 p.p.m. is interpreted as 0·18 lb/10^6 ft^3 or 290 mg/100 m^3.

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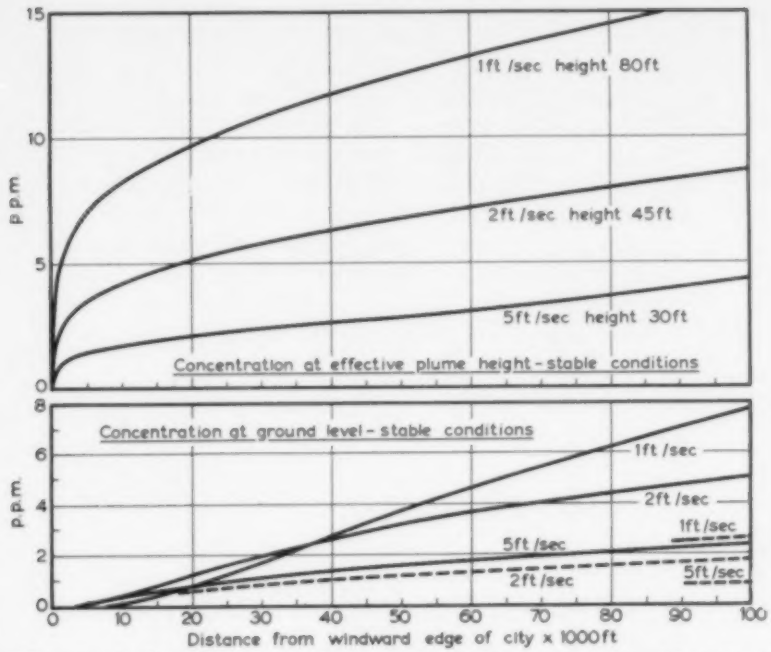


FIG. 1. SO_2 concentrations due to domestic fires under stable atmospheric conditions for different wind speeds for cities up to 100,000 ft across. Broken curves obtained by simplified "cone" formula.

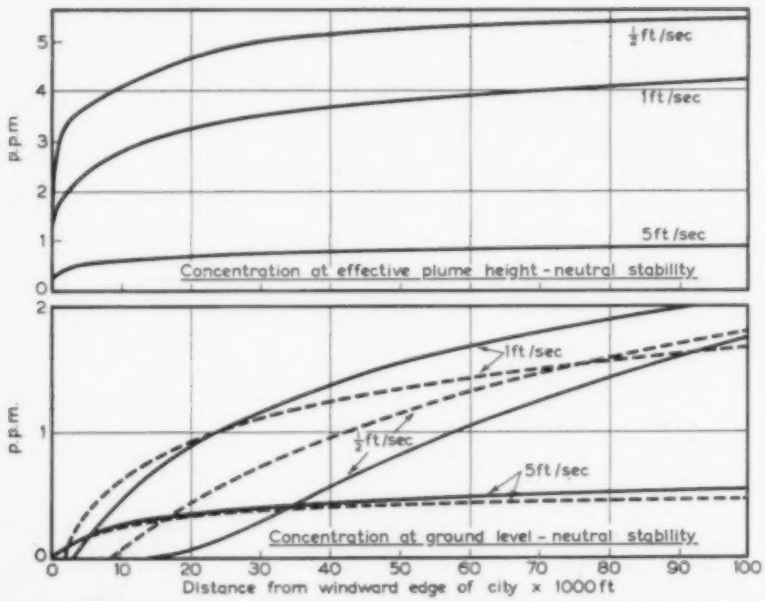


FIG. 2. SO_2 concentrations due to domestic fires under neutral atmospheric conditions for different wind speeds for cities up to 100,000 ft across. Broken curves obtained by simplified "cone" formula.

VOL.
1
958/9

the concentration at plume height is enhanced by recently emitted sulphur dioxide. Fig. 1 also illustrates the important diluting effect of increasing wind speed.

Fig. 2 illustrates that, although ground-level concentrations build up nearer the windward edge of the town under neutral conditions, they do not rise to anything like the same ultimate level. Moreover, low wind speeds are rare under neutral conditions.

Fig. 3 shows that as the wind speed rises above 3 ft/sec it dilutes the pollution under all conditions. As it falls below 3 ft/sec, under stable conditions, concentrations tend to rise to very high levels. However, under neutral conditions the plume rise due to buoyancy is so effective even for domestic chimneys that it more than compensates for the falling wind speed. This tendency of the plume rise due to buoyancy to ameliorate conditions of low wind speed is indicated even under stable conditions by the minima which appear in three of the curves.

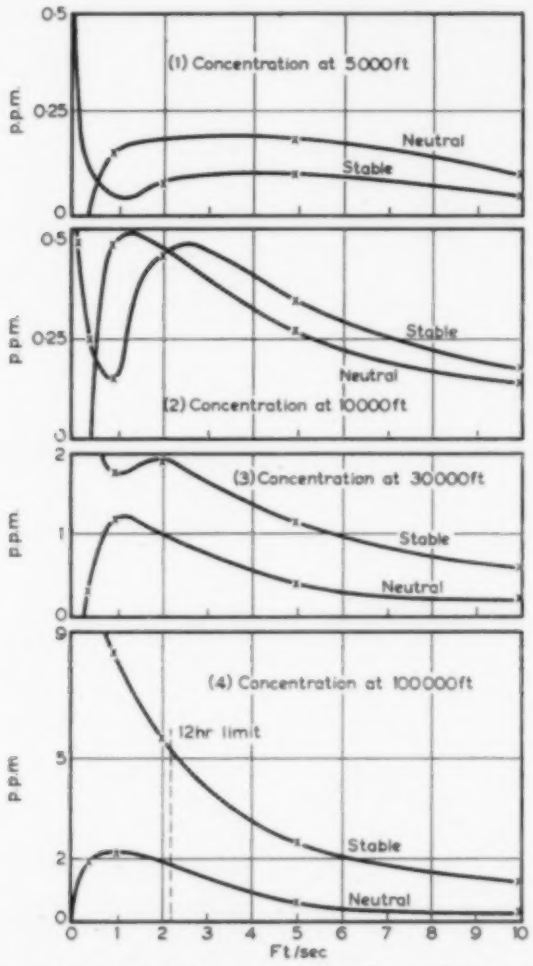


FIG. 3. Effect of wind speed on ground-level concentration at different distances from windward edge of city.

Its effectiveness is, however, mainly stifled by the stability of the atmosphere.

Fig. 4 shows that if a stable layer is limited in height it produces smaller concentrations than an infinite one. The differences are, however, small unless the effective chimney height approaches the top of the stable layer.

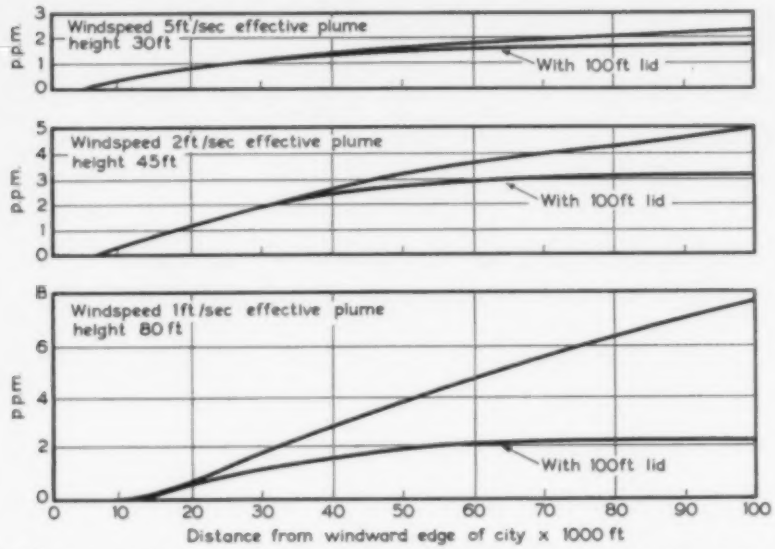

Windspeed 5ft/sec effective plume height 30ft
With 100ft lid
Windspeed 2ft/sec effective plume height 45ft
With 100ft lid
Windspeed 1ft/sec effective plume height 80ft
With 100ft lid
p.p.m.
Distance from windward edge of city x 1000 ft

FIG. 4. SO_2 concentration in a city with a stable layer 100 ft thick compared with a stable layer of unlimited height.

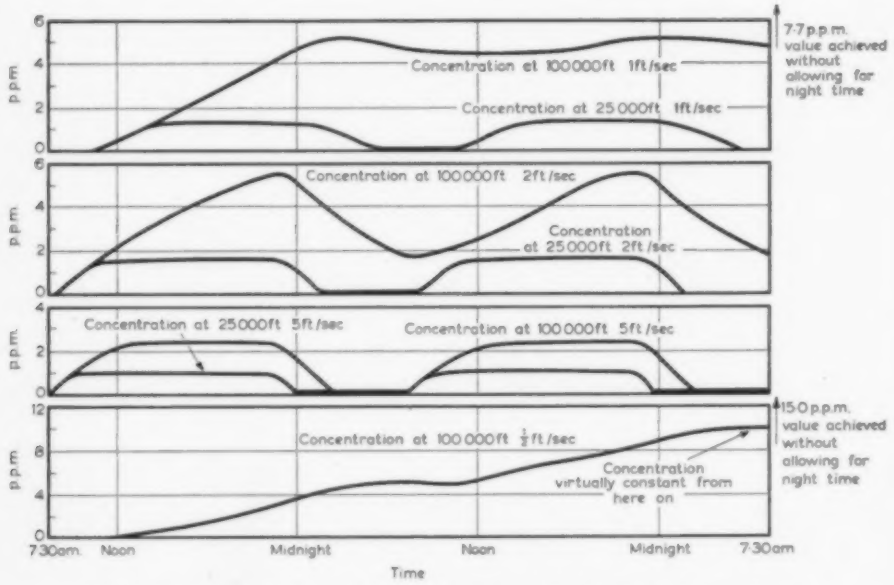

Concentration at 100000ft 1ft/sec
Concentration at 25000ft 1ft/sec
7·7 p.p.m. value achieved without allowing for night time
Concentration at 100000ft 2ft/sec
Concentration at 25000ft 2ft/sec
Concentration at 25000ft 5ft/sec
Concentration at 100000ft 5ft/sec
Concentration at 100000ft ½ft/sec
Concentration virtually constant from here on
15·0 p.p.m. value achieved without allowing for night time
p.p.m.
7·30am Noon Midnight Noon Midnight 7·30am
Time

FIG. 5. Diurnal cycle of ground-level SO_2 concentrations under stable conditions.

Fig. 5 shows that the night period has a strong effect in reducing the maximum concentration obtained with low wind speeds. The concentration at 100,000 ft when the wind speed is 1 ft/sec is 40 per cent less than it would be if the day rate of emission continued all night. It also shows that under these conditions the concentration does not vary greatly from day to night. With smaller distances and greater wind speeds, however, the night period has the obvious effect that it reduces night-time concentrations, but does not affect day-time concentrations very markedly.

The figure also shows that many hours are required for concentrations to build up when the wind speed is low.

Comparison with the Leicester Survey

In the Leicester Survey (D.S.I.R., 1945) it was shown that pollution concentrations did not vary inversely with wind speed but, apparently, inversely as the square root of wind speed. A possible reason for departure from the first power law is shown quite clearly in Fig. 3. For wind speeds below 5 ft/sec the effective plume height is increasing and ground-level concentrations are thereby decreased. Ultimately as

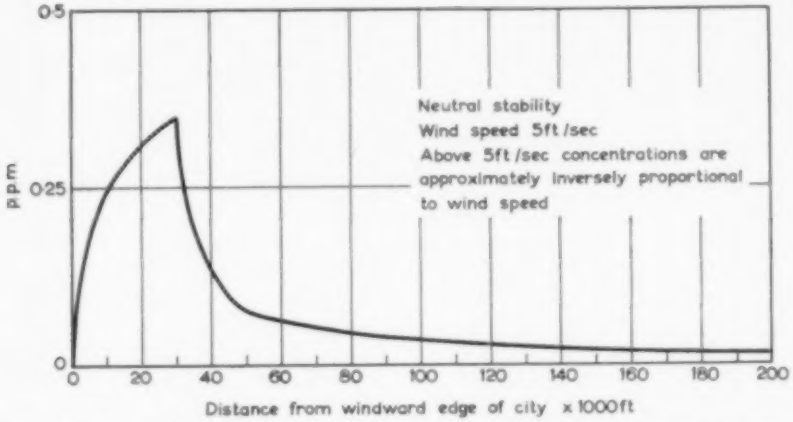
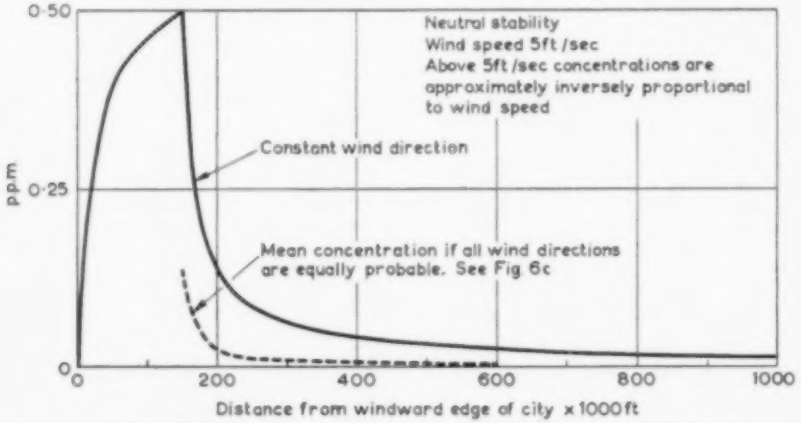
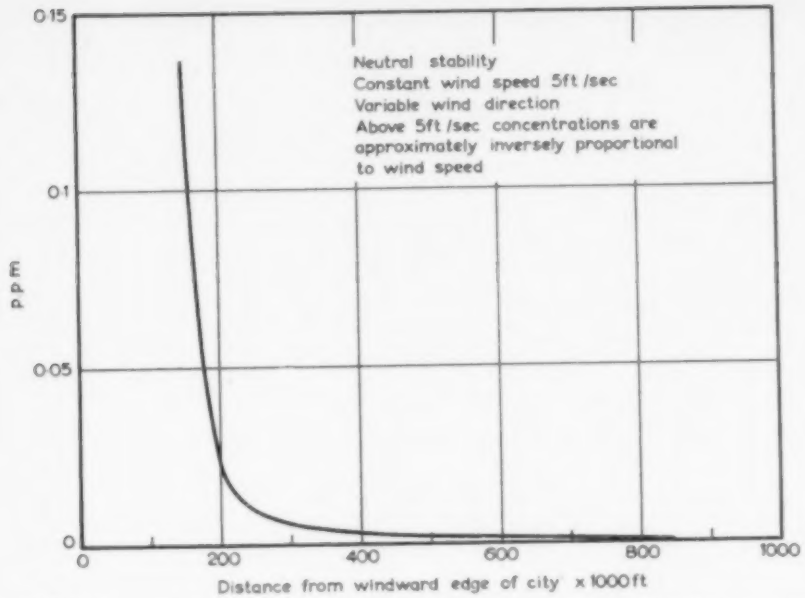


FIG. 6 (a) Rise and fall of pollution level with a steady wind blowing past a 30,000 ft city.



(b) Rise and fall of pollution level with a steady wind blowing past a 150,000 ft. city.



(c) Fall of mean pollution level outside a 150,000 ft city if all wind directions are equally probable.

VOL. 1 958/9

wind speeds tend to zero the general trend is actually reversed and concentrations actually fall. With domestic sources the effect becomes noticeable below 5 ft/sec. However, with the larger factory sources the " turnover " velocity will be in the range 5–20 ft/sec and overall there will be a flattening of the wind velocity effect.

The Survey also showed that maximum pollution levels occurred near the centre of the city and not at the extreme edge. This is in contrast to the results shown in Figs. 1 and 2. However, these figures assume uniform density of emission over the whole city.

If the figures used for integration are examined it is seen that, although sources from all distances combine to produce the concentration at a point, it is the relatively near sources (<10,000 ft) which produce the major part of the integrated figure. It follows that, if the intensity of emission drops off progressively from the centre of the city outwards, in the suburbs on the lee side the concentration will fall because the local contribution is falling off.

Fig. 7 shows the concentrations which obtain in a city of 30,000 ft diameter when the rate of emission rises linearly from the edges of the city to the centre. The calculations are based on " integrated line sources ". This cannot strictly be applied to a city with circular symmetry. The effect shown in Fig. 7 will probably be somewhat greater in practice. The average rate of emission along the central track considered is kept equal to the rate of emission already taken for Greater London; the rate at the city centre is twice the average. The result was obtained by adjusting each of the increments of concentration previously calculated according to the emission rate at its place of origin before integrating numerically. The shape of the curve is in general agreement with the results obtained in the Leicester Survey.

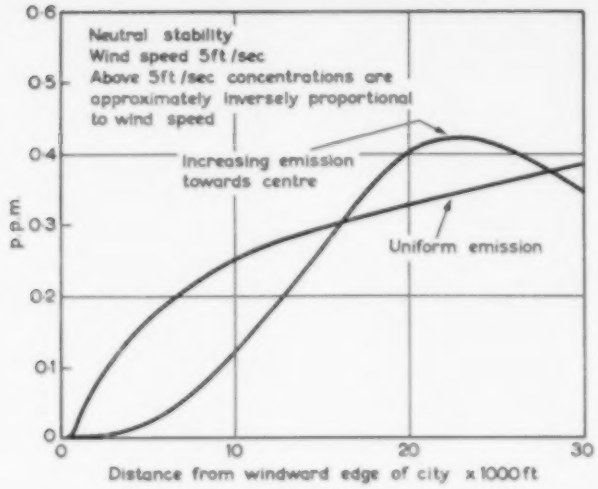


FIG. 7. Pollution level across a 30,000 ft city with increasing emission towards the centre.

Comparison with measured results in London

Taking the winter average for volumetric sulphur dioxide measurements for Camberwell, Chelsea, City, Deptford, Greenwich, Lambeth, Shoreditch, Southwark, and Westminster for 1954–5 (D.S.I.R., 1955), the weekend average is 0·114 p.p.m., the week-day average is 0·145 p.p.m. The former figure corresponds to 4·6 mg/100 cm² per day as measured by sulphur candle (D.S.I.R., 1945).

From Fig. 2 the concentration at 100,000 ft with a 5 ft/sec wind speed is 0·565 p.p.m. This result has assumed a factor of 1·6 because coal is mostly burned by day and 1·5 for cold weather conditions. For average winter conditions the figure becomes 0·235 p.p.m. Assuming that the concentration is inversely proportional to wind speed, and taking average wind frequency figures, we have the figures given in Table 3.

TABLE 3

Wind speed (ft/sec)	Frequency %	Concentration	F × C
0–6	19	0·235	4·4*
6–18	54	0·098	5·3
18–35	26	0·049	1·3
35–56	1	0·026	0·03
		Total	11·03

The mean winter concentration = 0·11 p.p.m.

The closeness of this figure to 0·114 is fortuitous. The figure obtained depends on the average figure assessed for the first group of wind speeds and this is problematical.

* The mean in this range is assessed arbitrarily at 5 ft/sec to allow for the fact that the inverse law does not apply below 5 ft/sec.

However, it is clear that there is good agreement between measured and calculated results.*

Comparison with point sources

The wind blows from a point source towards one particular sector relatively rarely. In consequence concentrations averaged over a period are at least an order lower than those experienced in the actual plume. This does not apply to places near the centre of an area source because they experience no relief when the wind direction changes.

Comparison with a single house

If a typical house is assumed to have four occupants it follows from the data already presented that its emission in cold weather will be $1{\cdot}7 \times 10^{-4}$ ft³ of SO_2 per sec. Using SUTTON's formula, with a wind speed of 5 ft/sec, and assuming again a chimney height of 30 ft, the *maximum* ground-level concentration is approximately 0·01 p.p.m. The corresponding *average* concentration for a city derived from Fig. 2 is 50 times as great. This ratio should be approximately constant with increasing wind speed.

Comparison with a power station

This comparison can only be made at a particular wind speed since the effect of wind velocity on a power station plume is very different from its effect on a domestic plume. HAWKINS and NONHEBEL (1955) stated that a power station burning 200 tons/hr with 1·5 per cent sulphur content with a 300 ft chimney will have a *maximum* instantaneous ground-level concentration of 0·32 p.p.m. in a 20 ft/sec wind. The maximum ground-level concentration averaged over a period with variable wind direction will be 0·015 p.p.m. It must be pointed out that in this case at lower wind speeds the concentrations will be *less*. Furthermore practical measurements (unpublished results) suggest this calculation is pessimistic.

The effect of industry

The assumption of uniform density of emission across the area under consideration is less valid for factories than for houses. Furthermore the effect of plume rise due to buoyancy is intermediate in its influence between the cases of the house and the power station. A detailed analysis will not therefore be attempted. However, if we assume (1) uniform distribution, (2) fixed plume height of 150 ft, (3) that industry has, in winter, an output equal to domestic fires (as is suggested by the Beaver Report), it follows that industry will increase concentrations, in a city the size of London, under average wind conditions, by 65 per cent. When the wind speed is low this figure will be less.

Pollution in the lee of cities

It is sometimes stated that the pollution from a city affects a large area of countryside in the lee of the city. This is supported by the comments of airmen that, from above, the smoke pall from cities can be seen for many miles downwind. The rate

* Using the conversion constant 1 p.p.m. = 290 mg/100 m³ (see Section 3) the calculated average winter concentration of smoke is 32 mg/100m³. The measured winter average for Chelsea, City, Deptford, Greenwich, Lambeth, Southwark, and Westminster for 1954–5 (D.S.I.R. *Report*, 1955) is 30 mg/100 m³ for the week-end and 40 mg/100 m³ for week-days. Again there is good agreement between measured and calculated results.

VOL. 1 58/9

at which ground-level concentration decreases outside the city limits is shown in Fig. 6 (a), (b) and (c).

It will be seen that the intensity of pollution drops off very rapidly, in marked contrast to the observations made from the air. It must be realized that, with a source of considerable width across wind, sideways diffusion largely cancels out. It is diffusion upward which reduces ground-level concentrations. Diffusion upward, however, has no effect on visibility from above downward since the observer is always looking through the pollution integrated with respect to height. Thence observations from above do not give a reliable indication of ground-level concentrations.

Furthermore, the concentrations calculated for a particular occasion are not significant unless the frequency of the occasion is borne in mind. Thus, while Fig. 6(b) shows that pollution from London may be measurable at a particular place 100 miles away on a particular day, the wind blows from London to that place so rarely that the contribution made by pollution from London is negligible, as shown in Fig. 6 (c).

The special case of prolonged atmospheric stability

If the results shown in Figs. 1 and 5 are applied to the notorious fog incident of December 1952 in London there is a marked contrast between measured and calculated results. The Kew Observatory of the Meteorological Office kindly supplied the information that for 5–8 December the average daily wind speeds were 0·5, 0·53, 0·57 and 1·6 ft/sec. The concentration to be expected from Fig. 5 is 9 p.p.m This is nearly an order higher than the measured concentration which rose only to about 1·5 p.p.m.

There is a further difficulty that the treatment adopted so far indicates a maximum concentration on the leeward edge of the city whereas the measured maximum is near the centre. This difficulty can be partly resolved by the argument used in discussion of the Leicester Survey results. It can be still further discounted by the knowledge that the wind direction during the period was variable so that there was no true leeward side. It follows that the distance used as abscissa in the graphs should be considered as the distance travelled by a quantity of air pursuing a random walk since it entered the city. In general the length of random walk will be a maximum in the centre of the city.

The contrast between measured and calculated figures is more difficult to resolve but it is almost certainly associated with the fact that prolonged periods of stability are invariably associated with fog.

The effect of fog on stable atmospheres

If a fog exists, it tends to lose heat by radiation from its top upward. It tends to check any radiation loss from the ground. It follows that a fog tends to become colder in its upper layers than lower down and hence it tends to destroy any stable temperature distribution existing within itself (and to engender a stable layer just above itself). Moreover, the colder air at the top of the fog tends to fall towards the ground and thereby keep the fog layer well stirred. In this system the ground-level air motions are interpreted as merely mixing movements and do not represent a true wind.

It is of interest to calculate the concentrations which will be obtained under such circumstances. The assumptions are that (a) the wind speed is zero, (b) the stable

layer above the fog is impenetrable, (c) there is efficient mixing throughout the fog layer and (d) the factor of 1·5 for cold conditions applies. The concentrations obtained are shown in Fig. 8. The important conclusions are that concentrations increase linearly with time and that they rise to 5–10 p.p.m. in 3 days. Neither of these agrees with observation.

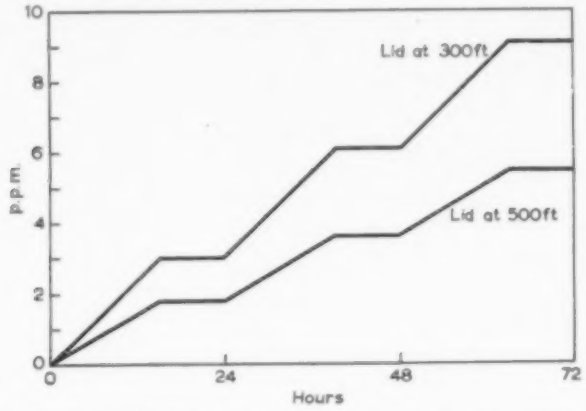


FIG. 8. Rise of concentration in a city with zero wind speed but mixing to a fixed height.

Although it must be agreed that fog *tends* to destroy a stable layer, there is no practical evidence that it always in fact succeeds. Information is unfortunately very scarce but evidence does exist that fog and stable layer can exist simultaneously, either because the original stable layer was so strong that it takes a long time for fog to break it down or because some other mechanism for forming stable layers (advection perhaps) is counteracting the fog effect.

There is a further effect of fog which is very relevant to the present discussion.

The effect of fog on pollution

It is known that sulphur dioxide dissolves in water. It is also known that, once dissolved, it oxidizes very rapidly to sulphuric acid. It follows that water droplets can remove considerable quantities of sulphur dioxide. (A similar argument can be made in the case of smoke.) It can be shown that the rate of diffusion of sulphur dioxide into fog droplets is extremely rapid. It is known that the oxidation rate of sulphur dioxide in water is also extremely rapid. In fact, these two processes are so fast in the laboratory that they would be expected to remove the bulk of the sulphur dioxide from the atmosphere and concentrations would be expected to be negligible.

This explanation of the discrepancy has the serious drawback that it succeeds too well. It appears that there must be some mechanism which controls either the dissolving of the sulphur dioxide in the droplets or the oxidation of the sulphur dioxide once dissolved. It is known that the oxidation of sulphur dioxide is a highly complex matter which can be accelerated and inhibited by a great range of substances and circumstances. It seems likely, therefore, that when sufficient chemical knowledge is available the discrepancies between the results calculated and the results measured may be resolved.

VOL.
1
58/9

In a recent paper by COUGHANOWR (1956) the oxidation of SO_2 in water droplets has been studied. In this particular case manganous sulphate was used as catalyst and under simulated fog-inversion conditions SO_2 was oxidized at 1 per cent/min.

Again it has been pointed out by L. G. AUSTIN in a private communication that collected particles and droplets from a fog sometimes have a net basic reaction. This implies that there are alkaline constituents of fog which could profoundly modify the persistence of SO_2 in the gaseous phase.

In any case, it appears that sulphur dioxide will have a limited life in a fog. The life of a particular SO_2 molecule will depend on its probability of diffusing to a particle able to absorb it. Thence the " life " will almost certainly be analogous to the " life " of a radioactive isotope, i.e. such that $n = N_0 e^{-t/T}$ where n is the number of molecules at time t and T is a characteristic constant.

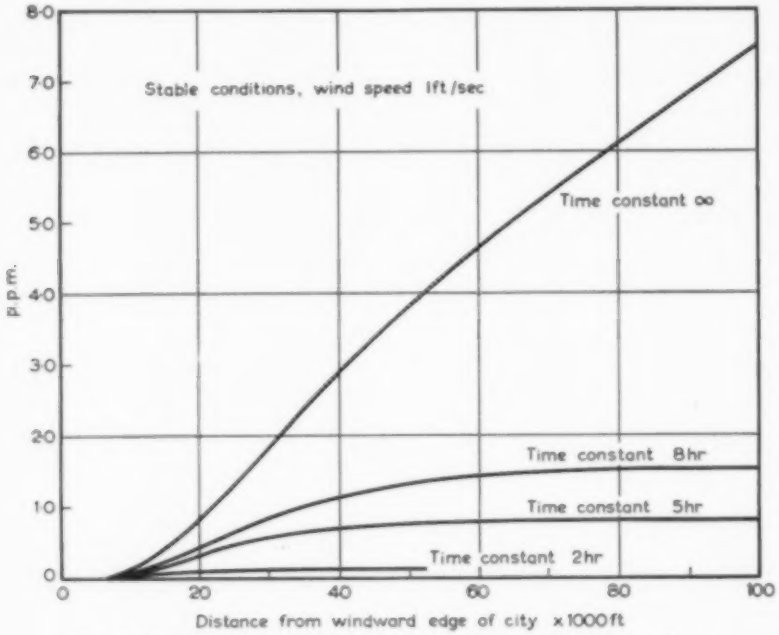


FIG. 9. The effect of limited life of SO_2 on calculated pollution levels.

It is impossible to estimate the probable value of this constant from available information. However, it is possible to demonstrate the effect produced when this constant has certain values. Fig. 9 shows the concentration curve for stable conditions with a wind speed of 1 ft/sec and the derived curves when the time constant of sulphur dioxide decay is 8, 5, and 2 hr. It is of interest to notice that with a time constant of 8 hr calculated figures agree with measured figures; and that concentrations reach an equilibrium figure relatively rapidly. It is interesting to notice that the limited life of sulphur dioxide not only reduces ground-level concentrations but also minimizes the effect of changing wind speed. The concentration at a given place tends to rise as the wind speed falls. It requires, however, a longer time to achieve its equilibrium value and this implies that more sulphur dioxide is lost by absorption

and oxidation. It follows that, while a fog persists, sulphur dioxide concentrations are very dependent on sulphur dioxide time constant and relatively independent of wind speed.

It is of course possible that there is a continuous removal of SO_2 coupled with complete mixing at all heights up to the fog top. In this case the time constant which reconciles measured and calculated figures for a fog rising to 500 ft is 20 hr.

It is of interest to know whether the ground-level concentration is kept down by mixing or by the removal of SO_2. A measurement of either the change of concentration with height or the change of temperature with height made during a fog will resolve the matter for that particular fog. If the temperature decreases with height more slowly through the fog than the wet adiabatic lapse rate, or if the concentration falls appreciably with height it can be assumed that complete vertical mixing is not operative.

CONCLUSIONS

Under conditions of neutral atmospheric stability it is possible to calculate the concentration of pollution caused by a city and obtain good agreement with observed results. The concentration produced at ground level by an area source at a distance x from its windward edge under conditions of normal stability can be given to a first approximation by

$$C_x = \frac{14W}{U}\left\{\ln y + \frac{1}{y} - \frac{1}{y^2 \times 2 \times 2!} + \frac{1}{y^3 \times 3 \times 3!} \cdots\right\}$$

where $y = \dfrac{0{\cdot}00165x^2}{h^2}$

W = average emission rate in ft^3/ft^2 sec

U = wind speed in ft/sec

h = effective chimney height in ft.

The concentrations of SO_2 produced at ground level by an area source such as a town are large compared with the concentrations produced by an individual source whether this is a house or a power station, particularly when concentrations are averaged over the normal range of wind direction. Concentrations fall very rapidly outside the city boundary, particularly when averaged over a range of wind directions.

Under prolonged stable conditions, if diffusion alone is considered, the concentrations calculated are far higher than those measured. It is suggested that under these conditions the SO_2 is absorbed by fog droplets and oxidized or neutralized. This, coupled with the subsequent descent of the fog droplets to the ground, effectively removes SO_2 and hence prevents the build up of SO_2 which would otherwise occur. A " time constant " of 8 hr reconciles measured and calculated results.

The results support the view that there will be no worthwhile reduction in ground-level SO_2 concentration in towns while the domestic grate continues to emit SO_2 at its present rate.

Acknowledgements—This paper is published by permission of the Director of the Central Electricity Research Laboratories. The author acknowledges the assistance of G. Spurr in providing meteorological information and in checking the computations, W. G. Cummings in confirming the rapid oxidation of SO_2 in solution, and Miss R. B. Bolt in carrying out some of the computations. He would also like to acknowledge the assistance of Dr. R. S. Scorer while the paper was being prepared for publication.

VOL. 1 58/9

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VOL
1
1958

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THE ATMOSPHERIC DIFFUSION OF GASES DISCHARGED FROM THE CHIMNEY OF THE HARWELL REACTOR BEPO

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(*Received* 17 *March* 1958)

Abstract—The 61 m chimney of the BEPO reactor discharges warm air containing a small amount of radioactive argon (^{41}A). This gas has been used as a tracer to study the diffusion of the plume in the atmosphere downwind of the chimney. Surveys have been carried out at ground level up to a distance of 10,000 m and, with instruments suspended from a balloon, up to a height of 300 m at a maximum range of 1000 m. The results have been correlated with the gradient of potential temperature in the atmosphere near ground level.

The effective height of the plume is found to depend on the wind velocity u and on the temperature gradient, having a mean value of 125 m under adiabatic conditions when $u = 7$ m/sec. The diffusion of the plume over the range studied occurs in three distinct phases. Near the chimney, the rate of vertical diffusion is about twice that in the horizontal direction as a result of the discharge conditions. As the plume diffuses towards ground level it enters a region dominated by building turbulence and the rate of diffusion in both directions is greatly increased. Finally, as it travels beyond the built-up area, the rate of diffusion reverts to that characteristic of diffusion over open country.

SUTTON's diffusion equations cannot be simply applied to this complex type of problem, but they provide a useful model for classifying the data, and effective values of the virtual diffusion constants C_y and C_z are derived for each stage of the diffusion process.

Under adiabatic and stable conditions, peak ground-level concentrations between $1{\cdot}3 \times 10^{-6}$ and $3{\cdot}5 \times 10^{-6}$ units/m^3 were observed at approximately 1000 m downwind with wind velocities in the range 6 to 12 m/sec and a chimney emission rate of 1 unit/sec. Under statically stable conditions no detectable concentrations were found on the ground within 10,000 m of the chimney.

This paper is a shortened version of an A.E.R.E. report (STEWART *et al.*, 1954).

VOL.
1
58/9

1. INTRODUCTION

MANY industries have to dispose of obnoxious gases and dusts by discharging them into the atmosphere, and the choice of suitable chimneys and discharge conditions to ensure that no unpleasant or hazardous concentrations arise at ground level is one that has to be made in advance by plant designers. Although the problem is a common one and of great economic importance, few measurements have been made of the diffusion of gases from isolated chimneys under operational conditions. Several theoretical papers have appeared over the past 20 years. BOSANQUET *et al.* (1950) have derived an expression for the rate of rise of the jet from a chimney resulting from the initial vertical momentum and excess temperature of the gases. BOSANQUET and PEARSON (1936) and, more recently, SUTTON (1947a, b) have derived semi-empirical formulae for the diffusion of gas or smoke in an idealized atmosphere in terms of certain parameters adjustable to suit varying degrees of atmospheric stability. One of the main problems has been the choice of values for these parameters, which can only be determined by direct experiment.

The chimney of the Harwell reactor (BEPO) provides a steady source of radioactive argon (^{41}A) formed when the natural argon present in the cooling air is subjected to

neutron bombardment in its passage through the reactor. Thus ^{41}A acts as a tracer whose detection and measurement in the atmosphere downwind of the chimney has made possible a study of the rate of diffusion of the plume under various atmospheric conditions. Measurements were made both in a vertical plane and at ground level. These confirmed an earlier finding that there is no health hazard at ground level from the BEPO discharge.

2. PROPERTIES OF ^{41}A

^{41}A decays with a half-life of 110 min, producing β-particles of maximum energy 1·17 MeV and γ-rays of energy 1·37 MeV. The β-particles have a maximum range of about 3 m in air, but the γ-rays are not so readily absorbed and have a "half-intensity" range of some 100 m. If a β-sensitive Geiger counter is placed in the centre of a large volume of air containing ^{41}A, the flux of γ-rays across the wall of the counter will be many times the flux of β-particles owing to their great range, and although the efficiency of such a counter for γ-rays is small ($\sim\frac{1}{2}$ per cent), the net result is that the γ-response of the counter may be comparable with that of the β. Thus, to measure the β-activity at any point in the plume, and hence to estimate the local concentration of the exit gases, it is necessary to carry out a differential measurement.

3. MEASUREMENT OF ^{41}A CONCENTRATION IN AIR

3.1 *Method of measurement and apparatus*

In the method adopted two identical B12E Geiger counters with separate battery-operated scaling units were used at each point. One counter was exposed to the atmosphere in the usual way and gave a combined β- plus γ-response. The second counter was covered by a p.v.c. shield designed to cut out all the 1·17 MeV β-particles while giving the same or very nearly the same γ-response as the unshielded counter. The difference in the counting rates of the two Geigers thus represented the activity due to the β-particles only.

The complete assembly is shown in Fig. 1 attached to the cable of the mobile barrage balloon used for the vertical surveys. The main unit consists of three boxes, two of which contain scaling units and post office registers while the third houses the batteries. The Geiger counters are mounted at the end of a 5 ft arm to reduce the shielding and scattering effects of the scaler assembly.

3.2 *Calibration*

Preliminary measurements showed that only those β-particles which originated within 7 ft of the Geiger counter penetrated its walls in significant numbers. The counter was therefore calibrated by placing it at the centre of a 15 ft diameter fabric balloon into which chimney gases were introduced in known dilution.

4. BASIC DATA

4.1 *Chimney constants*

Height of chimney	= 61 m (200 ft)
Internal diameter of chimney	= 3·5 m
Rate of efflux of cooling air	= $8{\cdot}9 \times 10^4$ g/sec
Velocity of gases at top of chimney	= 10 m/sec
Temperature of gases at top of chimney	= 50°C above ambient.

VOL.
1
958/9

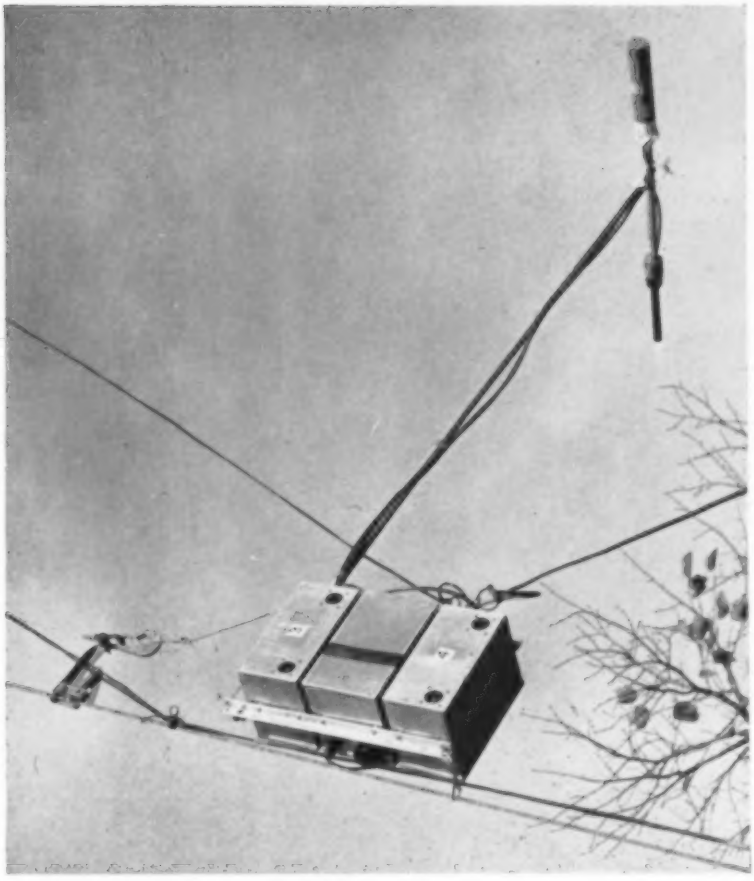

FIG. 1. Scaler and counter assembly on balloon cable.

VOL
1
1958/

4.2 *Description of site*

The BEPO chimney stands near the south perimeter of the Establishment which, at the time of the measurements, occupied an area of 0·2 mile². The boundary of the built-up area is shown diagrammatically in Fig. 2, in which the position of the chimney is clearly marked. The vectors **A** and **B** denote directions in which most of the ground-level surveys were carried out.

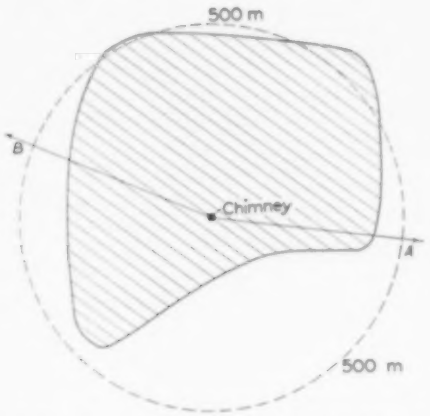

FIG. 2. Sketch of built-up area around chimney.

VOL.
1
58/9

The main buildings are between 8 and 16 m high. Those areas of the surrounding countryside in which measurements were made consisted of fairly flat farmland with few striking features.

5. METEOROLOGICAL MEASUREMENTS

The dilution of gases emitted continuously from a chimney depends on the mean wind velocity and on the degree of diffusion caused by the turbulence of the atmosphere. Since turbulence cannot be measured directly, it has been customary in this type of work to measure meteorological parameters which are known to be associated with the turbulent state of the atmosphere, notably the vertical gradients of temperature and wind velocity. These measurements were made in the present case with the primary object of correlating the ^{41}A data with RICHARDSON's number which is defined in terms of the two gradients (RICHARDSON, 1925). In the analysis of the results, however, a higher degree of correlation was obtained with the temperature gradient alone than with RICHARDSON's number, and the wind gradient measurements will therefore not be described.

During the first twenty-six surveys in the vertical plane, temperature measurements were made at heights of 61 m and 152 m by balloon psychrometers attached to the cable of the barrage balloon which supported the ^{41}A measuring instruments. The temperature difference between the two heights was measured to an accuracy of $\pm$0·35°F (standard deviation). This method of measurement required frequent inter-calibration of the thermometers and added greatly to the time required for a survey. For the remaining twenty-six vertical surveys, spot measurements were made by an observer of the temperature differences between the 9 m, 18 m and 27 m levels on a

wooden tower erected near A.E.R.E. and upwind of the prevailing wind direction. These temperature differences were measured by aspirated copper–constantan thermocouples and averaged over 10 min periods to give an accuracy of ±0·1°F. Finally, for the subsequent ground-level surveys, automatic temperature-measuring equipment was installed on a wooden tower to provide a continuous record of the temperature difference between heights of 9 m and 32 m (CROOKS and TOUREAU, 1953). The accuracy of measurement was again ±0·1°F.

Wind speed and direction records were provided by a Dines anemometer erected near the reactor at a height of 35 m above ground.

6. OBSERVATIONS IN THE VERTICAL PLANE

6.1 *Choice of experimental conditions*

The classical diffusion experiments with ground-level sources at C.D.E.E. Porton were carried out at selected times when the potential temperature gradient was very nearly zero, in order to reduce the number of variables and to obtain as consistent a set of measurements as possible (SUTTON, 1947). This method of selection was not practicable in the present experiments. The maximum number of measurements was made within an allotted period of time, irrespective of the prevailing temperature gradient. The only criterion adopted was that the wind direction should be steady in the sense that it showed no systematic change during the period required for an observation.

6.2 *The plume measurements: general experimental procedure*

The procedure in the vertical surveys was to mount up to ten of the double scaling units at suitable intervals along the cable of a mobile barrage balloon placed directly downwind of the chimney. The instruments could be started and stopped by a single switch at ground level but had in general to be brought down to ground level for reading and checking. Each vertical survey lasted between 10 and 30 min and generally smooth concentration curves were obtained over such intervals. The range of observation was restricted to a maximum of 650 m for the most part by the absence of suitable roads, but on a few occasions it was possible to exceed this figure.

In classifying the meteorological conditions accompanying each survey, the principle has been adopted that all differences of potential temperature over any particular height range have been classified as adiabatic when they lie within ± one observational standard deviation of zero. Thus between 9 m and 27 m, all potential temperature-differences between ±0·1°F have been classified as adiabatic. Observations lying outside these ranges have been classed as stable if the potential temperature-difference lies to the positive side and unstable if to the negative side.

6.3 *Description of the observed concentration curves*

Of the 53 successful vertical surveys, 33 were carried out under adiabatic conditions, 12 under unstable and 8 under stable conditions. In all cases corrections were made for the radioactive decay of the ^{41}A between the source and the point of observation and the recorded concentration figures are therefore applicable to any non-radioactive gaseous effluent. Full statistical details of each survey are given in the original A.E.R.E. report (STEWART *et al.*, 1954).

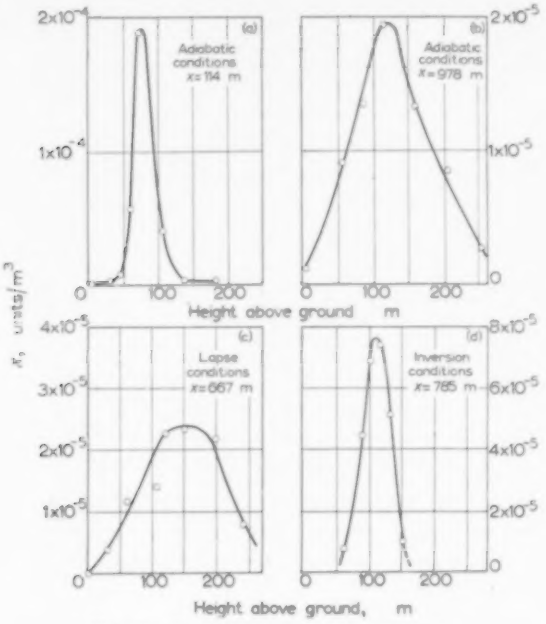

FIG. 3. Vertical cross-sections of plume.

The two concentration curves shown in Figs. 3(a) and 3(b) illustrate the expansion of the plume with distance and the gradual diffusion of the effluent gas to ground level under adiabatic conditions. In each case the observed concentrations have been normalized to a chimney output of 1 unit/sec. The curve of Fig. 3(c), indicating a relatively higher rate of diffusion, was obtained under unstable conditions. The adiabatic and unstable curves are of approximately Gaussian form, somewhat extended in the direction of increasing height. In contrast, curves obtained under stable conditions have a rather sharp cut-off, as is shown in Fig. 3(d).

6.4 *Method of analysis: the Sutton diffusion formulae*

The general aim in analysing the data is to express the results in terms of SUTTON's formulae for the diffusion of matter released by an idealized elevated point source (SUTTON, 1947a). This procedure is not valid close to the chimney, where the shape of the plume is much influenced by the diameter of the chimney and by the temperature and initial vertical momentum of the effluent gases. No expression exists for the rate of spread of the plume at close distances, but BOSANQUET *et al.* (1950) give formulae from which the locus of the centre of gravity of the plume may be calculated for a given set of output conditions.

The SUTTON formulae in their simpler form are summarized in the Appendix. The concentration at a distance x downwind of a continuous point source in the free atmosphere is given by the expression:

$$\chi = \frac{Q}{\pi C_y C_z u x^{2-n}} \exp - \frac{1}{x^{2-n}}\left(\frac{y^2}{C_y{}^2} + \frac{z^2}{C_z{}^2}\right) \qquad (1)$$

This equation implies that the horizontal and vertical cross-sections of the plume are Gaussian curves with standard deviations given by:

$$\sigma_y = \frac{1}{\sqrt{2}} C_y x^{1-n/2}, \qquad \sigma_z = \frac{1}{\sqrt{2}} C_z x^{1-n/2} \tag{2}$$

where C_y and C_z—SUTTON's virtual diffusion coefficients—and n are constants under fixed meteorological conditions. Although C_y and C_z are in theory deducible from observations of eddy velocities, no such measurements have been carried out at heights above a few metres and hence the validity of the values suggested by SUTTON for elevated sources has not been established. One of the primary objects of the present experiments was therefore to derive empirical values for these constants under various meteorological conditions.

SUTTON shows that n is related to the vertical wind gradient and may be determined by fitting the theoretical profile $u = u_1^{n/(2-n)}$ to the observed change of wind velocity with height. For adiabatic conditions he adopts a value of $n = 0{\cdot}25$ based on measurements made of the wind gradient between 50 and 150 ft over the aerodrome at Cardington (GIBLETT, 1932). The values suggested by SUTTON for unstable and moderately stable conditions are 0·20 and 0·33 respectively, although no reliable observational data can be quoted to support them. Values of 0·18, 0·14 and 0·30 for the three conditions were obtained from an analysis of the wind speeds measured at 9 m and 27 m above ground during the present surveys.

The three constants C_y, C_z and n provide SUTTON's equations with great flexibility in the matter of fitting experimental results. But this flexibility conversely implies that a wide range of associated values of C_y, C_z and n can be used to describe particular results with comparable accuracy. After consideration, it has been decided to use SUTTON's value of $n = 0{\cdot}25$ throughout this paper for all meteorological conditions. The choice of a single value for n has the advantage of simplicity in that the number of variables required to describe the results is effectively reduced by one. The actual value chosen has wide general acceptance under adiabatic conditions and, by using it, the deduced values of C_y and C_z will be automatically comparable with those of other workers.

6.5 *The values of C_y and C_z derived from the vertical surveys*

By fitting a Gaussian curve to each curve of concentration, a value of σ_z can be calculated for each set of measurements. The corresponding value of C_z can then be deduced by substituting for σ_z in equation (2), but since SUTTON's equations are strictly valid for a point source only, it is necessary to replace the BEPO source by an equivalent point source some distance upwind and to measure all distances from this new origin. The position of this origin can be roughly determined by the criterion that when $n = 0{\cdot}25$, σ_z should vary as $x^{0{\cdot}875}$. The calculated values of σ_z under adiabatic conditions can be shown to satisfy this criterion when the position of the equivalent point source is 56 m upwind of the actual source, and this adjustment has been used in deducing the values of C_z. Corresponding figures can be obtained for C_y but, since no direct measurements were made of the horizontal section of the plume, the effective values of C_y are computed from equation (2) of the Appendix which may be written in the form:

$$C_y = \frac{Q}{\pi \chi_m C_z u x^{2-n}} \tag{3}$$

All the quantities on the right-hand side of this equation have been either measured or calculated. If any particular survey has been off-axis the observed value of χ_m will be smaller than the true peak concentration, and the deduced value of C_y will be an overestimate. The computed values of C_y must therefore be regarded as upper limits only.

Under adiabatic conditions the values of C_z are distributed about a mean value of 0·20 m$^{\frac{1}{2}}$ with a standard deviation of $\pm$0·042 m$^{\frac{1}{2}}$ or $\pm$21 per cent. In SUTTON's theory for an idealized source, C_z is independent of the wind velocity u but in these experiments a clear correlation was found between the two quantities. This is expressed by the regression equation:

$$C_z = 0{\cdot}108 + 0{\cdot}013u \tag{4}$$

which is significant at the 0·15 per cent level. Using this equation the observed values of C_z have been adjusted to take account of the relative differences in u but as a result the standard error is only reduced from 23 per cent to 19 per cent which is much greater than the estimated maximum experimental error of $\pm$9 per cent. Attempts to correlate the adjusted values of C_z with other meteorological parameters, including

TABLE 1. EXPERIMENTAL VALUES OF C_y AND C_z AT VARIOUS DISTANCES

1	2	3	4	5	6	7	8	9
	Range (m)	Vector direction	Sampling time (min)	Conditions	C_y	C_z	Standard sampling time of 40 min	
							C_y	C_z
Vertical surveys	150–1000	All directions	15–20	Unstable	0·15	0·25	0·16	0·27
				Adiabatic	0·09	0·20	0·10	0·22
				Stable	0·09	0·11	0·10	0·12
Ground surveys (β)	590–620	A	40	Adiabatic and unstable	0·46	—	0·46	—
	880–1050	B	40	Adiabatic and unstable	0·28	0·32	0·28	0·32
	1200	A	40	Adiabatic and unstable	0·33	—	0·33	—
Ground surveys (γ)	2400–2800	A	15	Adiabatic and unstable	0·23	—	0·26	—
	6000–9700	A	15	Adiabatic and unstable	0·16	0·17	0·18	0·19
Ground surveys (β)	1000–10,000	A	60	Stable	—	<0·04	—	<0·04

VOL. 1 58/9

some derived from the Dines anemograph trace, yielded nothing of significance. The gas temperature and velocity of emission were constant throughout the experiments. Yet the available evidence supports the conclusion that the spread in the values of C_z is due to some definite external factor rather than to some unexpected experimental errors. For example, the value of C_z obtained on surveys made less than 1 hr apart are consistent with a standard deviation of ± 6 per cent between successive readings, which is more in accord with the estimated experimental errors.

The average value of C_y under adiabatic conditions is 0·09 m$^{\frac{1}{2}}$ and although this is to be regarded as an upper limit it is considerably smaller than the mean value of $C_z = 0{\cdot}20$ m$^{\frac{1}{2}}$. This result would not be expected if the diffusion of the plume had been due to atmospheric turbulence alone since at heights above 20–25 m there is a strong evidence for believing that the horizontal and vertical components of eddy velocity are equal (BEST, 1935). It must be presumed therefore that the relatively high effective value for C_z is a result of the mode of discharge of the gases from the chimney. In a gusty wind, the rate of rise of the plume will vary with the magnitude of the gusts (Section 6.7) and on a time-average observation this will produce a wider vertical section than the instantaneous one. In addition, as the plume rises it is subjected to shearing forces across its boundary and these, together with the action of thermal currents, will also have the effect of increasing dispersion in a vertical direction.

In unstable conditions, the mean values are $C_y = 0{\cdot}25$ m$^{\frac{1}{2}}$ and $C_z = 0{\cdot}15$ m$^{\frac{1}{2}}$. In stable conditions, the corresponding figures are 0·11 m$^{\frac{1}{2}}$ and 0·09 m$^{\frac{1}{2}}$.

The results are summarized in Table 1.

6.6 *The effect of sampling time*

SUTTON (1947b) has pointed out the importance of distinguishing between the " instantaneous " and " time-mean " aspects of a cloud or plume at short distances from the source. At any instant, the plume section will be comparatively narrow with a high peak value on the instantaneous axis. If measurements are made over periods of several minutes, the curve of concentration across any section of the plume, while retaining the same general shape, will be somewhat broader than the instantaneous curve and will have a lower peak value. This is due to the swinging of the plume over a wider region in response to longer period eddies than those which, in the main, affect the instantaneous aspect.

The Porton ground-level observations discussed by SUTTON are all based on sampling times of 3 min, experience having shown that the front covered by the cloud increased fairly rapidly as the sampling time increased up to 2 min, and thereafter only slowly. The present series of measurements in the vertical plane are based on sampling periods of 10–30 min, and in comparing the values of C_y and C_z with those proposed by SUTTON it is important to estimate to what extent sampling time affects the measured peak concentration and the dimensions of the plume at heights of the order of 120 m.

A number of surveys was carried out under adiabatic conditions with the particular object of studying the short-period variations of concentration on the time-mean axis of the plume. Four instruments were modified to send their signals to ground level and were mounted on the balloon cable so as to make it virtually certain that one of them would be close enough to the time-mean axis to provide a reliable figure for the axial concentration characteristic of the period of measurement T. The readings of

VO
1
1958

each instrument were noted over successive intervals of 1 min throughout the period of observation. The position of the " time-mean " axis was defined by the instrument which gave the highest average reading over the period T. The concentrations measured on this instrument over successive minute intervals were combined in groups to give the mean concentrations over convenient sub-intervals of time τ within T. The highest of these values was selected as the characteristic axial concentration for the period τ. Twenty-six surveys of this type were carried out in which ratios r of the characteristic axial concentrations were determined for a number of values of T and τ. The averaged data are presented in Fig. 4 in which the values of r are plotted against T/τ on a log–log scale. It follows from Fig. 4 that the measured axial concentration in the plume is inversely proportional to the fifth root of the time of sampling. Since the axial concentration varies inversely as the product $C_y C_z$ it is to be expected that C_y and C_z will be directly proportional to the tenth root of the time of sampling.

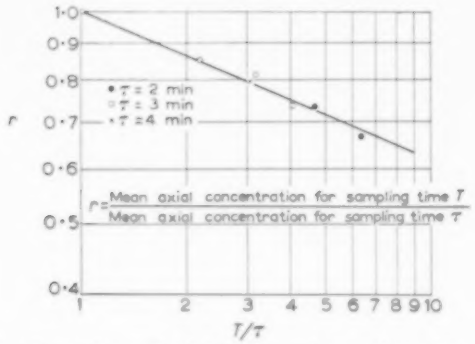

FIG. 4. Dependence of axial concentration on time of sampling.

At a height of 100 m, SUTTON (1947) reasons that $C_y = C_z = 0{\cdot}07$ m$^{\frac{1}{2}}$ for a 3 min sampling period under adiabatic conditions, although he can offer no direct evidence to confirm this value. This is equivalent to a figure of $C_y = C_z \approx 0{\cdot}08$ m$^{\frac{1}{2}}$ for a 15 min sampling period, which may be compared with our observed values of $C_y = 0{\cdot}09$ m$^{\frac{1}{2}}$ and $C_z = 0{\cdot}20$ m$^{\frac{1}{2}}$. It has already been argued that the high observed value of C_z may be due to the initial efflux conditions.

6.7 *Effective height of plume*

The effective height of the plume at any distance is defined as the height above ground of the point of maximum concentration.

The observed heights under adiabatic conditions have been classified according to the prevailing wind speeds and are plotted against distance in Fig. 5 for wind speeds in the three groups 4–5·5, 5·5–8·5 and 8·5–12 m/sec. Although the individual points were obtained over a period of 2 months they are clustered fairly consistently around the mean curves with only two exceptions. The dotted curves also shown in the diagrams are theoretical curves computed from the formulae given by BOSANQUET *et al.* (1950). Agreement is good at the lowest wind speeds, but the general tendency is for the theory to underestimate the rise of the plume.

Nearly all the measurements in unstable air were made at wind speeds in the range

VOL. 1 958/9

5·5–8·5 m/sec. The observed plume heights showed a much higher degree of scatter than in the corresponding adiabatic case, the points being confined between the adiabatic curve of Fig. 5 and a curve representing twice as much rise about the point of discharge.

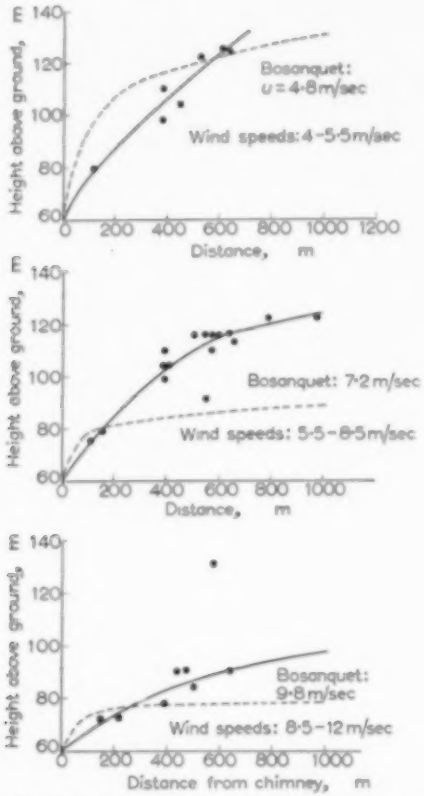

FIG. 5. Plume heights under adiabatic conditions.

The number of observations in stable air is too few to allow general conclusions to be drawn, except that the scatter on both sides of the adiabatic curve is very large. In these conditions the height of the plume is a function of both the degree and the height of the inversion, and the meteorological observations were not detailed enough to investigate possible relationships.

7. GROUND-LEVEL SURVEYS

7.1 *Experimental procedure*

A number of measurements was made at ground level with the portable scaling units, but the sensitivity of the Geiger counters limited the useful range of observation to some 2000 m downwind. Beyond this distance calibrated γ-ray monitors were used. Useful data can be obtained from γ-ray measurements when the lateral spread of the plume is large compared with the " half-intensity range " of the γ-rays. Applying this principle to the BEPO plume, it was shown that the form of the cross-wind

concentration curve, and hence C_y, could be measured at ranges beyond 2000 m, and the absolute gas concentration at distances greater than 6000 m.

Surveying was confined to the two principal directions **A** and **B** shown in Fig. 2. A period of observation of 40 min was used to obtain the required accuracy on the β-surveys but 15 min were sufficient with the γ-monitors.

7.2 *Crosswind surveys: values of* C_y

Thirty-five crosswind surveys were carried out at ranges between 590 m and 9700 m under both adiabatic and unstable conditions, and a typical concentration curve is shown in Fig. 6. Values of C_y were determined in the usual way and the average figures at various distances are given in Table 1. These averages have been computed without discriminating between adiabatic and unstable conditions since there appeared to be no clear correlation between C_y and temperature gradient. To simplify comparison, all the observed values of C_y, together with those of C_z, have been adjusted in the last two columns of the table to correspond to a common period of observation of 40 min.

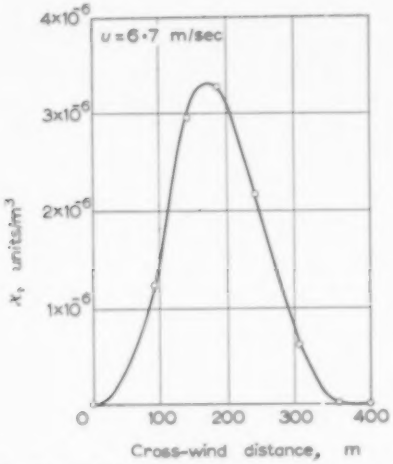

FIG. 6. Crosswind concentration curve at ground level.

It is immediately obvious that the ground-level values of C_y, particularly at a range of 600 m, where the mean value is 0·46 m$^{\frac{1}{2}}$, are much higher than those deduced from the vertical surveys. To investigate the reason for this apparent anomaly, observations of the turbulence pattern around the Establishment were carried out with two recording bi-directional wind-vanes of the Sheppard type (DEACON, 1953). This type of light-weight vane is pivoted universally at its centre of gravity and responds to wind-direction changes within a solid angle about the mean wind direction. A pen, mounted at one end of the moving arm of the device, records these changes of direction continuously on a stationary chart, and the mean width of the complex trace can be used as a measure of the turbulence in the atmosphere. Simultaneous records were obtained with one of the vanes placed upwind of the Establishment and the other about 100 m downwind of the built-up area. The difference between the records was very marked, the angular spread of wind direction being on average 2·5 times greater

on the downwind vane. The greatly increased turbulence is due to the disturbance caused by the buildings to the normal pattern of wind flow.

It is to be expected that, as the underside of the plume diffuses downward into the region dominated by building turbulence, its rate of expansion will be very high for a period, but as it travels beyond the limit of the built-up area, this rate will progressively decrease until it ultimately reaches the value associated with flow over open country. The apparent values of C_y should therefore decrease with distance. This is confirmed by the observations in direction **A** where the mean value of C_y varies from 0·46 m$^{\frac{1}{2}}$ at 600 m to 0·18 m$^{\frac{1}{2}}$ at an average distance of 8000 m. On the hypothesis that the turbulence caused by the buildings has effectively disappeared at 600 m, i.e. 200 m downwind of the limit of the built-up area, and that the diffusion from then on is controlled by the open-country value of $C_y = (C_y)_0$, a value of $(C_y)_0 = 0{\cdot}15$ m$^{\frac{1}{2}}$ can be deduced from the data.

7.3 *Downwind surveys: values of* C_z

Seven downwind surveys were carried out in day-time, mostly under unstable conditions and a typical concentration curve is shown in Fig. 7. In all cases, the downwind distance x_m of the point of maximum concentration lay within the range 980 to 1100 m. Including results of crosswind surveys carried out at approximately 1000 m, the peak ground-level concentrations lay between $1{\cdot}3 \times 10^{-6}$ and $3{\cdot}6 \times 10^{-6}$ units/m^3 for wind velocities in the range 6 to 12 m/sec.

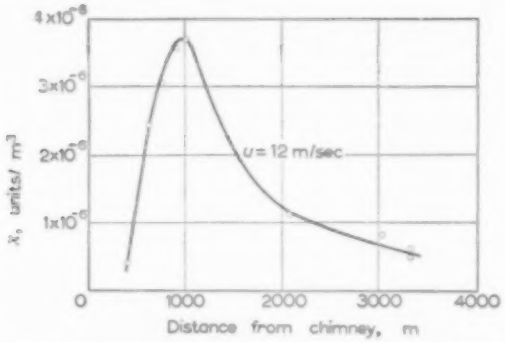

FIG. 7. Downwind concentration curve at ground level.

C_z is related to x_m and the effective height of the chimney by equation (7) of the Appendix. Choosing a value of $h = 135$ m appropriate to the unstable conditions of these surveys, an effective value of $C_z = 0{\cdot}32$ m$^{\frac{1}{2}}$ is obtained. This is only slightly higher than the value derived from the vertical surveys. An effective value of $C_z = 0{\cdot}19$ m$^{\frac{1}{2}}$, adjusted to a sampling period of 40 min, can be obtained from the surveys in the range 6000–9700 m using equation (5) of the Appendix. As in the case of C_y, the effective value of C_z decreases with distance downwind and the true value of C_z appropriate to diffusion over the open country can be deduced to be $C_z = 0{\cdot}17$ m$^{\frac{1}{2}}$. As expected, this is very nearly equal to the open-country value of $C_y = 0{\cdot}15$ m$^{\frac{1}{2}}$.

Six surveys were carried out in stable stratified air. A van was fitted with γ-ray equipment which enabled the presence of the plume overhead to be detected even when the concentration of radioactivity at ground level was negligible. At several distances,

β-measuring instruments were deposited at the points where crosswind γ-surveys had indicated peak values. Frequent surveys were made with the γ-equipment during the 60 min β-measuring periods to check that the mean position of the plume had not shifted. In no single case was any measurable β-activity found at ground level. This means that no concentrations greater than 2×10^{-7} units/m^3, the limit of sensitivity, were found within 10,000 m of the chimney. Even with the smallest values of C_z found in the vertical surveys, measurable maxima would have been expected between 4000 m and 5000 m downwind. Since no maxima were encountered within 10,000 m, it follows that the effective value of C_z over this range is less than 0·04 m$^{\frac{1}{2}}$. The higher mean value of 0·09 m$^{\frac{1}{2}}$ observed nearer the chimney in the vertical surveys is almost certainly a consequence of the mode of discharge.

7.4 *Comparison of ground-level results with independent experimental data*

No experimental results obtained under similar conditions are available for direct comparison with the BEPO ground-level measurements, particularly in the vicinity of the built-up area. The " open-country " values of $C_y = 0{\cdot}15$ m$^{\frac{1}{2}}$, $C_z = 0{\cdot}17$ m$^{\frac{1}{2}}$ may, however, be tentatively compared with the results of experiments conducted over similar ranges with ground-level sources.

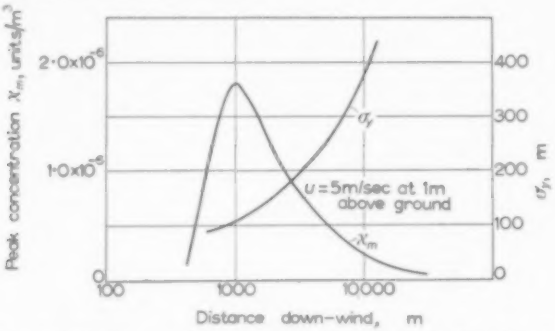

FIG. 8. Mean ground-level values of χ_m and σ_y in direction **A**.

CALDER (1948) has summarized all the Porton experimental results obtained with ground-level point sources over level stretches of downland on Salisbury Plain under adiabatic conditions. For a wind velocity of 1 m/sec and a sampling period of 4 min, the average value of the peak concentration at 1000 m is $1{\cdot}7 \times 10^{-4}$ units/m^3 for unit output per second. It follows from SUTTON's equations that the average value of the product $C_y C_z$ in the Porton experiments at 1000 m is 0·021 m$^{\frac{1}{2}}$. This is equivalent to $C_y C_z = 0{\cdot}034$ m$^{\frac{1}{2}}$ for a sampling period of 40 min, which implies that C_y and C_z are of the order of 0·18 m$^{\frac{1}{2}}$. This compares well with the mean value of 0·16 m$^{\frac{1}{2}}$ deduced from the present measurements.

Some experiments with ground-level sources were carried out over the Wiltshire Downs by C.D.E.E., PORTON (1949) in which the range of measurement was extended to 6 miles. The equivalent values of C_y and C_z at 5000 m, corresponding to a sampling period of 40 min, were 0·25 and 0·28 m$^{\frac{1}{2}}$ respectively. These are much higher than those obtained by CALDER at 1000 m and in the BEPO measurements at greater ranges. The explanation of the discrepancies may lie in the topography of the country over which the measurements were made.

VOL. 1 58/9

8. CONCLUSIONS

It has been shown that the dispersion of the gases emitted from the BEPO chimney presents a complex problem whose solution cannot be simply expressed in terms of any known theory. The conditions of discharge lead to a plume whose effective height and vertical dispersion in the early stages of travel are both dependent on wind speed. As the plume diffuses towards ground level it enters a region of high building turbulence where the lateral diffusion rate in particular is greatly increased. When the plume travels beyond the edge of the built-up area, its rate of diffusion reverts to that characteristic of travel over open country. This dependence on efflux conditions and on surrounding buildings, restricts the degree to which the results can be generalized.

Despite this, the experiments have yielded enough empirical data to allow predictions to be made of the concentration levels to be expected, not only from the BEPO chimney, but also from other chimneys erected on the same site, to a degree of accuracy sufficient to meet most requirements.

Since the rate of diffusion between chimney and ground is not uniform, SUTTON's equations cannot be rigorously applied to any of the ground-level observations described in this report. But these equations are still capable of describing the form of the crosswind and downwind curves obtained experimentally and in the absence of a more general theory it seems reasonable to express the results in terms of these equations, choosing appropriate values of C_y and C_z at each distance. C_y and C_z then cease to have the significance of SUTTON's virtual diffusion coefficients and are simply to be regarded as adjustable constants.

The most important quantity normally required in the practical case is the ground-level concentration. The BEPO ground-level results have been roughly summarized in Fig. 8 in which the average values of the peak concentration and the standard deviation of the crosswind concentration curve are plotted against distance downwind. The figures are valid for a surface wind speed of 5 m/sec at a height of 1 m above ground and a sampling time of 40 min. The concentration at any distance may be greater than the plotted figure by a factor of 1·5 under day-time conditions, while the lower limit (in stable conditions) is zero. The value of σ_y is subject to a variation of ± 25 per cent about the mean curve.

Acknowledgements—We would like to thank Dr. F. PASQUILL and the Meteorological Unit at A.E.R.E. for practical help and valuable discussion on the meteorological aspects of the work, also the Director, A.E.R.E. for permission to publish this shorter version of our Harwell report.

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LIST OF SYMBOLS

Symbol	*Meaning*	*Units*
x	distance downwind from chimney	m
y	crosswind distance from plume axis	m
z	distance above ground	m
h	height of emitting source, effective height of chimney	m
u	wind speed	m/sec
Q	source strength	units/sec
$\chi(x, y, z)$	concentration at the point (x, y, z)	units/m^3
χ_m	a peak value of the concentration	units/m^3
σ_y, σ_z	standard deviation of concentration curve in y, z direction	m
C_y, C_z	Sutton's virtual diffusion coefficient in y, z direction	m$^{\frac{1}{2}}$
n	Sutton's wind profile parameter	—
x_m	distance of maximum ground concentration	m

APPENDIX

Sutton's Equations for the Diffusion of a Plume

1. *Continuous point source in the free atmosphere*

The concentration χ at any point downwind of a continuous point source placed at $x=0$, $y=0$, $z=0$ in *free space* is given by:

$$\chi(x, y, z) = \frac{Q}{\pi C_y C_z u x^{2-n}} \exp\left\{-\frac{1}{x^{2-n}}\left(\frac{y^2}{C_y^2}+\frac{z^2}{C_z^2}\right)\right\} \tag{1}$$

On the axis of the plume ($y=0$, $z=0$) the peak value of $\chi=\chi_m$ is then given by:

$$\chi_m = \frac{Q}{\pi C_y C_z u x^{2-n}} \tag{2}$$

2. *Continuous point source above ground*

For a point source situated at a height h above ground,

$$\chi(x, y, z) = \frac{Q \exp(-y^2/C_y^2 x^{2-n})}{\pi C_y C_z u x^{2-n}} [\exp\{-(z-h)^2/C_z^2 x^{2-n}\} + \\ + \exp\{-(z+h)^2/C_z^2 x^{2-n}\}] \tag{3}$$

where the origin is taken at ground level, vertically below the source.

3. *Concentration at ground level due to elevated source*

When $z=0$,

$$\chi(x, y, 0) = \frac{2Q}{\pi C_y C_z u x^{2-n}} \exp\left\{-\frac{1}{x^{2-n}}\left(\frac{y^2}{C_y^2}+\frac{h^2}{C_z^2}\right)\right\} \tag{4}$$

From symmetry considerations, the peak value of the ground-level concentration will lie on the line $y=0$, $z=0$. The concentration along this line is

$$\chi(x, 0, 0) = \frac{2Q}{\pi C_y C_z u x^{2-n}} \exp\left(-\frac{h^2}{C_z^2 x^{2-n}}\right) \tag{5}$$

VOL.
1
58/9

This has a maximum value χ_m given by

$$\chi_m = \frac{2Q}{e\pi uh^2} \cdot \frac{C_z}{C_y} \tag{6}$$

at a downwind distance x_m where

$$x_m = (h/C_z)^{2/(2-n)} \tag{7}$$

VO
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1958

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A STUDY OF THE RADON CONTENT OF GROUND-LEVEL AIR AT HARWELL

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(*Received* 24 *February* 1958)

Abstract—The radioactive gas radon enters the earth's atmosphere as a natural emanation from many rocks and soils. During a period of a year continuous measurements were made of the radon in the atmosphere near ground level at Harwell by drawing air through a moving filter strip and measuring the radioactive disintegration rate of the radon decay products thus collected.

The observed concentrations appear to be closely connected with atmospheric stability, being high when the gradient of potential temperature is positive. A marked diurnal variation is observed closely following a similar variation in the gradient of potential temperature. The average concentration over the year was 64 pc/m³ and the maximum recorded 386 pc/m³.

1. INTRODUCTION

In large concentrations, for example in uranium mines, radon and its radioactive decay products are a potential health hazard. However, in the normal atmospheric concentrations expected at A.E.R.E., Harwell these radon products are a problem only in that they interfere with the routine air-sampling techniques which are a part of the Health Physics control system.

In 1950 an investigation was undertaken to measure continuously the radon concentration at A.E.R.E. and to assess its variation. The method used was to draw air through a moving strip of Whatman No. 41 filter paper and measure the β-activity of the radon decay products thus collected by a G.M.4 end-window counter placed immediately above the air orifice. A calibration enabled the results to be converted to atmospheric concentrations of radon. The experiment lasted from October 1950 to October 1951.

Recently a more detailed consideration of the results has been undertaken, particularly of the diurnal variations and their connexion with atmospheric stability. This is presented here and fuller details are contained in an A.E.R.E. report (GALE and PEAPLE, 1958).

2. RADON AND ITS DAUGHTER PRODUCTS

Radon is the gaseous daughter product of radium, which is widely distributed in the earth's crust. It is continuously produced at a steady rate by the radioactive decay process and makes its way into the atmosphere by seeping through fissures in the earth or more rarely via mineral springs.

The successive disintegration processes of radon can be shown diagrammatically as follows, where the particle accompanying each decay process is indicated, together with the half-life of the process.

$$\mathrm{Rn} \xrightarrow[(3{\cdot}83\ \text{days})]{\alpha} \mathrm{Ra}A \xrightarrow[(3{\cdot}05\ \text{min})]{\alpha} \mathrm{Ra}B \xrightarrow[(26{\cdot}8\ \text{min})]{\beta} \mathrm{Ra}C \xrightarrow[(19{\cdot}7\ \text{min})]{\beta} \mathrm{Ra}C' \xrightarrow[(\text{very short})]{\alpha} \mathrm{Ra}D \xrightarrow[(22\ \text{years})]{\beta} \text{etc.}$$

VOL.
1
958/9

It is found that, due to continual removal by rain, the β-activity of Ra*D* and its daughter products is negligible compared with that of its predecessors (BLIFFORD *et al.*, 1952). Thus the general picture is that only Ra*B* and Ra*C* produce β-particles and that because their half-lives are short compared with that of radon their decay rate is very soon in secular equilibrium with that of the radon.

Hence measurements of the Ra*B* and Ra*C* concentration in air enable an estimate to be made of the concentration of the parent radon.

3. APPARATUS

Air was drawn through a 1 in^2 orifice containing a metal grid over which a $1\frac{3}{8}$ in. wide strip of Whatman No. 41 filter paper was driven at a constant speed of 1 in/hr, the air flow keeping the paper flat against the grid. A G.M.4 end-window β-counter was fixed symmetrically over the orifice with its window parallel to and at a distance of about 6 mm from it. The G.M.4 was connected to a counting rate meter the output of which was fed through a buffer amplifier to a four-point recorder. The counter was surrounded as far as possible by 2 in. of lead, to minimize the effect of background radiation.

The whole apparatus, together with a small electric heater, was mounted in a louvered box placed near ground level below a caravan housing the rest of the equipment, the filter strip being 10 in. above ground level. The caravan was situated in the middle of the airfield at A.E.R.E.

The pressure drop across the paper was measured by a mercury manometer the level of which was recorded on one point of the recorder and the manometer reading was interpreted in terms of air flow by calibrating the system periodically with a standard orifice. The mean rate of air flow for the experiment was about 50 l/min.

4. COLLECTION EFFICIENCY OF PAPER

When radon decays to radium *A* the resulting atom usually attaches itself to an atmospheric condensation nucleus, a particle of the order of 0·01 to 0·1 μ in diameter (WILKENING, 1952). Presumably in its further decays to Ra*B* and Ra*C* it remains attached to such particles. We must thus consider the efficiency of the Whatman paper, which was chosen for its mechanical strength and availability in roll form, for the collection of these condensation nuclei. The method adopted was to compare the amounts of β-active radon decay products collected under similar conditions on Whatman paper and on an asbestos paper (supplied by C.D.E.E., Porton) which is known to have a better than 99 per cent efficiency for the retention of condensation nuclei (CHAMBERLAIN, 1957). Circles of paper 4·5 cm in diameter were used in each case in exactly similar set-ups side by side and air drawn through for the same period in each case, usually 1 hr, the total amount of air being measured. The air velocity was chosen to be similar to that through the filter strip. The β-activities collected on the papers were measured on standard G.M.4 counting sets, and corrected for the longer lived activities contained in the air and the different counter efficiencies. Then the total radon decay product activities collected per unit air flow on each paper were compared.

Two sets of comparison runs were made, one set from 0900 to 1000 hr each day and one set from 1500 to 1600 hr each day. For each set of runs the efficiency of the Whatman paper relative to that of the asbestos paper varied from about 65 per cent to about

100 per cent spread in a random fashion about an average of 85 per cent. Detailed comparison of the pair of decay curves from any one run showed no significant differences, indicating that the relative amounts of Ra*A*, Ra*B* and Ra*C* collected by each paper were the same.

Measurements with a Pollak condensation nucleus counter showed that about 65 per cent of condensation nuclei were retained by the Whatman paper (WIFFEN, 1957), and this corresponds to the lowest value found above for the relative efficiency. Presumably, if the Ra*A* remains unattached, or is attached to a large particle, the efficiency is greater than this and may be 100 per cent (this is to be expected from the theory of action of filter papers) and this explains the higher values obtained. Thus the efficiency of collection of the Whatman paper varies with the concentration of the atmospheric condensation nuclei, and is apparently randomly distributed about the mean value of 85 per cent. This value has been applied to all the continuous strip observations, and thus an individual reading may be up to 20 per cent wrong, but averages of these readings over a sufficiently long time should be correct.

5. THE STATE OF EQUILIBRIUM OF THE RADON DAUGHTER PRODUCTS

In converting radon decay product concentrations into equivalent radon concentrations, the assumption has been made that the products are in equilibrium with the parent radon.

However, if fresh radon is introduced into an atmosphere, it takes about 100 min for the Ra*B* and Ra*C* concentrations to reach 80 per cent of the equilibrium value. Thus it is possible that this assumption is not always valid, and some measurements were made to check this.

The experiment consisted of drawing air through a filter paper, generally for 1 hr, then counting it with a G.M. tube and observing the manner in which the activity decays. Given the time of collection and knowing the relative penetrating powers of the β-particles from Ra*B* and Ra*C* through the counter wall, one can calculate the decay curve to be expected for various postulated states of equilibrium of Ra*A*, Ra*B*, and Ra*C* in the atmosphere. Then by a statistical analysis one can determine which of these states is the best fit to the experimental observations.

Of the ten observations where there was sufficient initial activity to carry out such an analysis, seven showed that the products were all in equilibrium with the radon; one gave a result implying that the concentration had changed during the collection period (although the collection was made on an occasion when this seemed unlikely) and the other two showed that the decay products had not yet reached equilibrium.

These results are similar to those of OKABE (1956) and imply that in general the assumption that the products are normally in equilibrium with radon in the atmosphere is justified. This is in agreement with the observations of TSIVOGLOU *et al* (1953) on the conditions when non-equilibrium occurrence is likely.

6. CALIBRATION

A point source of ^{134}Cs (chosen because its β-energy is similar to that of Ra*B*) was first counted in defined geometry on an E.H.M.2 counter to determine the disintegration rate of the source. It was then mounted on the centre of the filter strip and moved in steps to simulate a line source 1 in. long below a principal axis of the G.M.4 window. The geometrical efficiency of this line source was then deduced.

VOL.
1
58/9

Such a line source was mounted transversely on the filter paper and moved in steps from the leading edge of the orifice to the point 2 in. further on where the counting efficiency became negligible, the absolute efficiencies of each of the step positions being determined with respect to the principal axis efficiency already determined.

For given air concentrations of Ra*A*, Ra*B*, Ra*C* and given airflow, a calculation was made of the β-disintegration rates of the Ra*B* and Ra*C* collected on a strip element for each of the step positions. These amounts were weighted according to the geometrical efficiencies already determined and then integrated to give the counting rate due to a complete strip of paper passing across the orifice in the given conditions. This calculation showed that in equilibrium conditions, with 10 pc of radon per m^3 of air and an air flow of 50 l/min the counting rate would be 5·21 counts/min at a strip speed of 1 in/hr.

It also showed that this value would not be reached until several hours after the airflow started but that in 1 hr 98·6 per cent of the value is reached. (This is a function of the half-lives involved and the counter and orifice geometry.) Similar considerations apply to a sudden change of concentration, there being about a 1 hr delay before the change is almost fully reflected in the counter reading. For this reason an air concentration deduced from a chart reading at a particular time is appropriate to a time 1 hr earlier, and in all the tables, figures, and discussion allowance has been made for the delay.

In the worst non-equilibrium case mentioned in the previous paragraph, the radon concentration would be underestimated by about a factor of 2. This is not serious, particularly when considering averaged readings, as these conditions do not frequently occur.

7. RESULTS AND DISCUSSION

After the first few months of operation it was apparent that there was in general a marked diurnal variation in the concentration. For the subsequent observations continuous records of wind velocity and temperature gradient were taken, using an existing available installation. The temperature gradient measurements were made

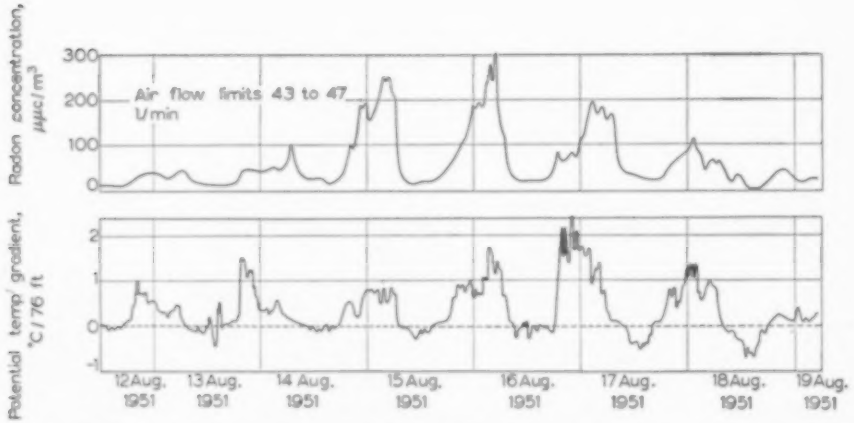

FIG. 1. Records of radon concentration and potential temperature gradient for period 1200 hr 12 August 1951 to 0500 hr, 19 August 1951.

between the levels of 32 and 108 ft on a tower on the airfield and the results displayed on another similar recorder, as described by CROOKS and TOUREAU (1953).

A typical extract from the records is shown in Fig. 1, in which the variation of radon concentration in the air is compared with that of the potential temperature gradient. It will be seen that high radon concentrations are associated with potential temperature gradient inversions, when the increased atmospheric stability would reduce the upward diffusion of radon emanating from the soil. A feature of all the observations is that the radon concentration begins to rise at very nearly the same time as the gradient of potential temperature changes from negative to positive values, although the subsequent reduction after the peak is more irregular.

TABLE 1. AVERAGE CONCENTRATIONS AND TEMPERATURE GRADIENTS (February–October 1951)

Hour of observation	Number of observations	Average radon concentration (pc/m³)	Average potential temperature gradient (per 76 ft)
1	163	74·9	0·375°C
2	163	79·9	0·410
3	163	83·4	0·425
4	162	87·0	0·390
5	160	85·0	0·352
6	158	79·4	0·276
7	155	73·7	0·114
8	137	67·3	0·047
9	131	57·7	−0·057
10	130	53·1	−0·121
11	134	45·8	−0·158
12	141	41·9	−0·160
13	136	38·6	−0·193
14	137	36·2	−0·193
15	147	34·2	−0·180
16	166	38·4	−0·111
17	170	39·7	−0·015
18	167	44·8	0·111
19	167	49·6	0·287
20	166	56·9	0·353
21	164	61·2	0·399
22	166	67·7	0·426
23	163	66·2	0·394
24	162	69·3	0·375

For the period from February to October 1951, temperature gradient measurements were available and where concurrent records existed the concentrations and corresponding potential temperature gradients were averaged hour by hour throughout the day and the results are given in Table 1 and Fig. 2. It will be seen that there is a marked diurnal variation of concentration with a maximum average value of 87·0 pc/m³ at 0400Z and a minimum of 34·2 pc/m³ at 1500Z. The diurnal variation is similar to that of the potential temperature gradient but lags behind it by about 1 hr, in contrast to the behaviour in individual cases at the onset of an inversion. In Fig. 2, to illustrate the spread of the results about the mean values, some typical " standard

errors " are shown. They amount to about 8 per cent of the mean value in each case, and arise almost entirely from actual variations of concentration.

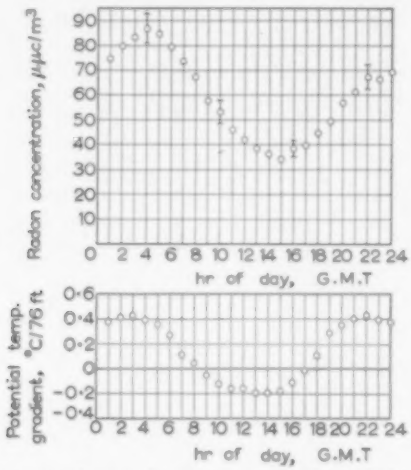

FIG. 2. Average concentrations and temperature gradients, February–October 1951.

Although it is reasonable to suppose that the high radon concentrations result from the atmospheric stability, as evinced by positive potential temperature gradients, other possible explanations of the observed diurnal variation of counting rate are that while the concentration remains constant, the collection efficiency changes throughout the day, or that the state of equilibrium of the radon and its products changes during the day. The first of these explanations is not compatible with the results of efficiency measurements, made at times when an appreciable difference in efficiency would be expected on this hypothesis. The second is unlikely because, although the average

TABLE 2. AVERAGE CONCENTRATIONS: ALL OBSERVATIONS

Month	Number of observations	Average radon concentration (pc/m³)
October, 1950	144	145·5
November	324	72·9
December	329	47·8
February, 1951	540	45·6
March	458	64·4
April	106	27·0
May	442	38·5
June	487	51·7
July	695	63·8
August	625	42·1
September	481	63·8
October, 1951	222	212·7
Total	4853	63·5

concentrations vary by only a factor 2·5 from maximum to minimum, the individual hourly concentrations vary from 4 to 386 pc/m³ of radon, and these variations would be difficult to explain on a non-equilibrium hypothesis.

It is difficult to draw any definite conclusions about seasonal variation trends as only 1 year was considered. In this year the maximum readings occurred in October and the minimum about April, but these variations again simply appear to follow the changes in average potential gradient for the corresponding periods. The results are given in Table 2.

There was no significant correlation between the activity and the amount of dust collected by the filter, and no apparent connexion between air concentration and wind velocity.

The average concentration of radon over the whole year was 64 pc/m³. This should be typical of open country in the south of England, away from granite areas and towns, which are usually associated with higher concentrations.

8. CONCLUSION

An analysis has been made of the diurnal variations of atmospheric radon concentration deduced from Ra*B* and Ra*C* activity and the variations have been connected with those of the atmospheric temperature gradient. It is concluded that the variations almost certainly reflect the true radon concentration variations. On the average the concentration varies during the day by a factor of 2·5. The average concentration over a year was 64 pc/m³ and the maximum recorded 386 pc/m³. Some figures are given of seasonal variation.

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VOL.
1
58/9

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SMOKE POLLUTION AND HOUSEHOLD COSTS

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(*Received* 18 *March* 1958)

Abstract—A social survey in Chesterfield Rural District shows that the household expenditure on cleaning varies by a factor of 2 according to the amount of pollution.

INTRODUCTION

CHESTERFIELD Rural District has a population of 92,920, the major part of the population living in fairly large villages. The western side is the more rural in character.

The survey to be described covered four villages all lying between Chesterfield Corporation Borough and the Sheffield City Boundary. Barlow and Holmesfield* are villages situated in a purely agricultural and residential area, Renishaw is close to an ironworks and slag crushing plant and Killamarsh is a colliery village 2 miles from Renishaw. The survey was undertaken because of many complaints received from Renishaw.

The average monthly deposit in tons/mile^2 at Barlow and Renishaw was as follows:

	Barlow	Renishaw
1955	9·29	73·60
1956	8·80	96·95

No pollution measurements were available for Killamarsh but direct observation suggests that the amount of pollution there is intermediate between Renishaw and Barlow. An examination of the vital statistics of the three areas did not indicate any marked differences in their mortality rates. It was thought however that there might be significant differences in the amounts spent on household cleaning. Various factors, of course, would be relevant to the amount spent, such as the type of work done by the wage earners, the size of the household and whether or not washing was sent to the laundry.

METHOD

The investigator visited certain houses taken at random in the Renishaw and Killamarsh districts and talked with the tenants about cleaning costs. From this pilot survey, the results of which were not used in the final analysis, a schedule of questions was drawn up.

From the current electoral roll, a 20 per cent sample was extracted for Renishaw, a 25 per cent sample for the Westhorpe area of Killamarsh and a 33 per cent sample of the more densely populated hamlets in the parishes of Barlow and Holmesfield. Shops and business premises were excluded and also cases where housewives were

* Referred to subsequently as Barlow.

vague, or where special circumstances were present, for example, where a pensioner was living alone and the relatives were doing the laundry and cleaning, and cases where the laundry was sent out.

The investigator obtained the *weekly amount* of toilet and household soap, soap powders, soap flakes, detergents, etc. used and worked out the cost afterwards.

The prices are those ruling at the time of the first survey. An attempt was made at first to assess the housewifery standards, but this was rather difficult as the information was often given on the doorstep, and in any case it was felt that this was not necessary as a *random* sample of houses ensured that a representative number of households of different standards were included.

The approximate number of houses in each district of the areas covered is shown below:

Barlow and Holmesfield	230
Killamarsh (Westhorpe area)	440
Renishaw	580

Renishaw, as already mentioned, suffers from pollution from blast furnaces and from a slag crushing plant. Killamarsh is about 2 miles to the north and both areas have a large population of coal miners.

Barlow and Holmesfield are rural villages with no nearby industry and have a mixed population.

Table 1 sets out the details of the visits for each district covered.

TABLE 1. ANALYSIS OF VISITS

	Barlow	Killamarsh	Renishaw	Total
Successful	47	89	91	227
Out	16	9	6	31
Refused	2	0	3	5
Laundry sent out	8	5	11	24
Unsatisfactory	0	4	2	6
Shops etc.	1	2	2	5
Total	74	109	115	298

TYPES OF WORK

In assessing whether a man had a clean or dirty job, it was decided that as far as his *home* was concerned he was considered to have a clean job if he could have a bath before leaving his work, therefore, miners who had pit-head baths came into the category of " clean job ".

The analysis by district and by clean or dirty job is shown in Table 2.

It is noteworthy that Barlow, an agricultural and residential area, had a higher proportion of wage earners employed on " dirty jobs ". The fact that coal miners who take advantage of the pit-head baths were classed as having a clean job, as far as the home is concerned, increased the proportion of clean jobs in Renishaw and Killamarsh.

VOL. 1 58/9

TABLE 2. ANALYSIS OF WORK—WAGE EARNERS

	Barlow		Killamarsh		Renishaw	
	No.	Per cent	No.	Per cent	No.	Per cent
Clean	30	50·8	87	71·8	79	59·0
Dirty	29	49·2	34	28·1	55	41·0
Total	59		121		134	

CURTAINS

An attempt was made to assess the frequency of washing curtains in the three districts but the investigator's lack of knowledge of materials rather hampered him. The term " net or other light-weight materials " was adopted. Households having none of this type were not counted in the survey. It is also to be noted that information given on this point may have been biased by local customs or considerations of prestige.

TABLE 3

	Barlow		Killamarsh		Renishaw	
	No.	Per cent	No.	Per cent	No.	Per cent
Under 3 weeks	6	7·9	51	20·9	73	26·1
Over 3 weeks	70	92·1	193	79·1	207	73·9
Total	76		244		280	

Table 3 shows that curtains were washed much more frequently in the more polluted areas.

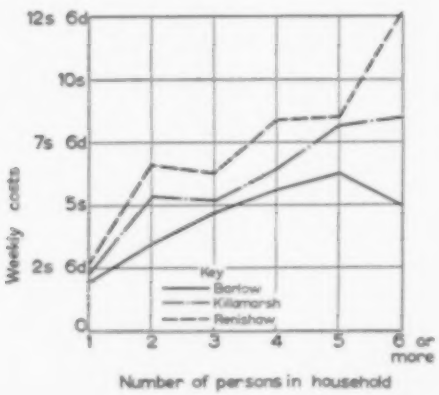

FIG. 1

Fig. 1 shows the weekly costs of cleaning materials in Barlow, Killamarsh, and Renishaw in families of different sizes. On an average the Renishaw housewife spends

3s. 1d. more weekly and the Killamarsh housewife 1s. 5d. more than her Barlow counterpart.

WATER HARDNESS

There are differences in the water hardness in some of the areas but the Water Engineer of the North East Derbyshire Water Committee states that the differences are not such as would make any significant differences in costs.

SUMMARY

Average weekly expenditure on cleaning materials by families in the villages covered by the survey were as follows:

Barlow	4s. 8d.
Killamarsh	6s. 1d.
Renishaw	7s. 9d.

From the above figures it would seem that housewives in the heavily polluted areas spend more money in cleaning materials than their counterparts in less heavily polluted areas.

It also follows that in the heavily polluted areas the housewife has to spend more time in keeping the house clean and that the wear and tear on fabrics is much greater than in the lightly polluted areas.

Acknowledgement—Mr J. Le Noury, B.Sc. (Econ.), part-time housing assistant, carried out the field work and tabulations.

VOL.
1
58/9

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Review Articles

ATMOSPHERIC CHEMISTRY

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Abstract—A network of about eighty stations has been established in north-west Europe for the study of airborne inorganic salts. Samples are taken in two ways, (a) by simple collection of rain-water, (b) by passing air through an absorbent solution. The sampling period is a calendar month. Rain-water is quantitatively analysed for S, Cl, NO_3—N, NH_3—N, Na, K, Mg, Ca, HCO_3, conductivity and pH, the air sample for S, Cl, NH_3—N, Na, K, Mg, and Ca.

In Scandinavia (the only region for which studies have yet been published) nearly all the airborne material is natural, and the great majority is of marine origin. Unexpectedly large amounts of sulphur and ammonia originate in the sea, presumably by the decay of organic matter. The amount of airborne material is greatest on the windward or south-west coast and decreases very rapidly inland; it seems to be lost mostly by direct deposition on the ground and vegetation, though some is carried upwards by turbulent diffusion. Washing-out by rain is not a principal cause of the decrease. It is remarkable that chloride disappears from the air more quickly than any other radical, showing that the sodium chloride is in some way decomposed. One possible explanation is that it is oxidized in the air, perhaps by ozone or sulphuric acid; and that the released chlorine or hydrochloric acid is rapidly absorbed at the ground or by vegetation.

The subject is closely related to atmospheric pollution, and it is obviously desirable that the two studies should have a common policy and, as far as possible, similar methods.

It has long been known that rain-water contains a number of inorganic salts in solution. The amounts are very small, only a few mg/l; in other words, 1 mm of rain brings down only a few mg of dissolved salts per 1 m² of ground. But since something like 5 per cent of this material consists of nitrogen in the form of nitrate or ammonium compounds, it has a small but quite significant value as fertilizer, and for this reason agriculturalists have studied the chemical constitution of rain-water for over a century.

The network of chemical sampling stations which now covers all north-west Europe grew from a study of this kind. The scheme originated with the Royal Agricultural College of Sweden, and the first intention seems to have been no more than a nation-wide survey of the nitrogen compounds brought down by rainfall. But the first results were so promising, both to the agriculturalists and to the meteorologists who collaborated with them, that it was soon decided to extend the scope of the work, and it has in fact continued to expand ever since: more and more stations have been added, sampling and analytical methods have improved, and the number of ions for which the analyses are made has increased. In 1951, a few stations were equipped to sample air, as well as rain-water, and this is now the usual practice. Finally, in 1954, an informal international agreement was reached (Eriksson, 1954) at Stockholm by which the sampling network was extended over all Scandinavia, Great Britain, the Netherlands, Belgium, and north-west Germany. At the same time a smaller, purely Scandinavian network was set up to measure carbon dioxide, but, as it has not yet begun to yield results of much interest, we shall not discuss it further. The larger network contains about eighty stations of which ten are in the United Kingdom. All the data from both networks are printed in full in *Tellus*, a quarterly Journal of Geophysics published in Stockholm.

VOL 1 1958

The sampling procedure is very simple (EGNER and ERIKSSON, 1955). The rain-water is collected by means of a funnel and bottle, while the air is drawn by a small electric pump through a dilute solution of nitric acid and hydrogen peroxide, at a rate of about 50 l/hr. All samples are taken for one calendar month. The rain-water is analysed for sodium, potassium, magnesium, calcium, ammonium, chloride, sulphur (sulphate and sulphite), bicarbonate, and nitrogen (nitrate and nitrite), and in addition its electrical conductivity and pH are measured. The air sample is analysed for all the same constituents except nitrate–nitrite and bicarbonate.

It will be seen that the sampling network examines only one aspect of the chemistry of the atmosphere. The subject has many other branches, concerned for example with the seasonal and geographical variations in the amount of ozone, oxygen, and carbon dioxide, with the nitrogen and CO_2 cycles, photochemical reactions in the upper air and the radioactive constituents of the atmosphere. But much of this research has been sporadic and isolated, and a principal aim of the Swedish workers has been to unite it all, around their own massive experiment, into a single coherent subject worthy of the general title " atmospheric chemistry ". In this, they have had considerable though by no means complete success. It is impossible, in a short article, to discuss all these varied activities, and only the results of the sampling network will be considered here. This is the part of the subject most closely related to atmospheric pollution. It will be apparent from what has already been said that the two subjects employ very similar sampling-procedures: the principal differences are that the atmospheric chemist makes much more detailed analyses both of the air sample and of the rain-water sample, and that he places most of his sampling units as far as possible from sources of smoke. The atmosphere he studies is therefore a " normal " one—the background against which all measurements of pollution must be assessed.

VOL.
1
58/9

This background has some curious features, few of which have yet been satisfactorily explained. There are of course some obvious and easily recognized sources of the principal airborne materials: the sea contributes sodium, magnesium, potassium and chlorine, and industrial areas yield sulphur and some chlorine. Ammonia is a product of animal life—there is a broad band of high ammonia values downwind of the dairy farming regions of Denmark—while calcium is largely derived from the erosion of limestone. All these are in accordance with the preconceptions with which one would naturally approach the subject, and all are to some extent confirmed by an examination of the published data; but they all need some qualification. The first and most obvious anomaly is the enormous quantity of sulphur found on windward coasts. The amount of sulphur deposited at Lista, on the south-west coast of Norway, is about 1·5 g/m² per year and is nearly twice as great as the amount brought down at Edinburgh! Clearly it cannot be a product of combustion, nor can it be the sulphate in sea-water: the amount is far too large in relation to the amount of sodium and chlorine to be explained in this way. It probably originates (MORDY, 1957) as hydrogen sulphide, being formed by the decay of marine vegetation on the Continental Shelf. At any rate it seems likely that more sulphur enters the atmosphere from the sea than from all the fuel burnt in the world.

The concentration of ammonia on the windward coasts is also surprisingly high, though not so strikingly so as that of sulphur. It is difficult to avoid the conclusion that considerable amounts of ammonia originate in or over the sea, though almost equally difficult to imagine how. It cannot come from the decay of organic matter

on the bottom of the sea, for so soluble a gas could not escape into the air in significant amounts. It has been suggested that it is formed by the decay of films of organic matter floating on the surface, but these scarcely seem capable of yielding the observed quantities.

New problems reveal themselves when one studies the history of the airborne material on its journey inland. The most striking fact is the rapidity with which the material is lost. By the time it has travelled 150 miles from the coast—a mere 10 hr in average conditions—four-fifths of it have disappeared. Moreover, the disappearance is selective. The concentrations of magnesium and potassium decrease fairly slowly, that of sodium more quickly, that of chlorine most quickly of all. On the windward coast, the ratio, weight of chlorine to weight of sodium in the air has, as a rule, much the same value (1·8) as it has in sea-water, as we should expect since, after all, both must enter the air as droplets of sea-spray. But far inland the ratio often falls below 1 and sometimes below 0·5.

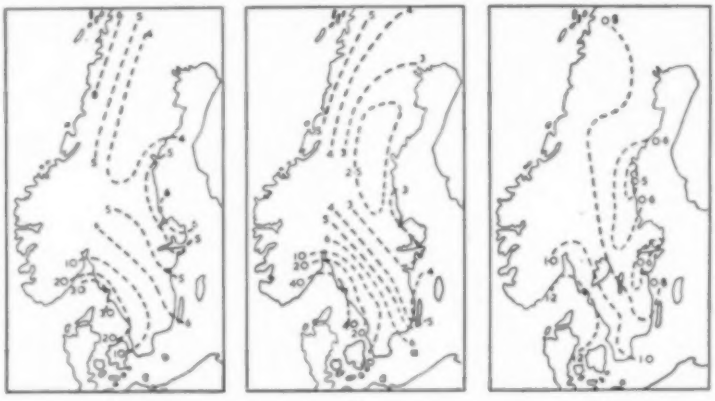

FIG. 1. Distribution in Scandinavia of the amounts of (a) sodium, (b) chlorine brought down by rain (kg/hectare per year). Diagram (c) shows the distribution of the ratio of chlorine to sodium in p.p.m. (from EMANUELSSON A., ERIKSSON E. and EGNER H. (1954), The composition of atmospheric precipitation in Sweden. *Tellus* **6**, No. 3, 261.)

The general nature of these changes is illustrated by Fig. 1. Map (a) shows the approximate annual amounts of sodium brought down by rainfall, in kg/hectare, in southern Sweden. Map (b) shows the corresponding deposits of chlorine, while map (c) shows the distribution of the Cl: Na ratio. The rapid decrease towards the east shown by (a) and (b) is in part due to the smaller rainfall in the east, but this does not of course affect map (c) and it is reasonably certain that a map showing the distribution of the mean Cl: Na ratio in the air would not differ very greatly from (c).

A great deal of discussion has centred on this double problem—the rapid and selective disappearance of airborne salts. So far as the general disappearance is concerned, it is easy enough to name all the agencies which can possibly contribute to it, and the only question remaining concerns their relative importance. Undoubtedly some part of the material is washed out by rain, but this will account for only a small fraction of the observed changes. For example, the average loss of material is still

quite large in dry months, when rain has fallen for perhaps only 4 or 5 hr altogether. Clearly washing-out cannot have contributed anything significant to the loss, since less than 1 per cent of the air has been washed at all. A second important way in which salts are removed is by direct deposition on various surfaces, especially leaves of coniferous trees. Rain-water dripping from trees almost always contains far more salt than does rain collected in the open. ERIKSSON (1955) has recently found further evidence of the importance of direct deposition; he has shown that the amount of chlorine carried away to the sea by Scandinavian rivers is something like double the amount deposited on the country by rainfall, as estimated from the data of the sampling network. A very small fraction of this excess may be due to chlorides eroded from rocks: the remainder is attributed by ERIKSSON to salt deposited on vegetation in the way just described—a result which, incidentally, emphasizes the well-known fact that a deposit gauge does not give a completely reliable measure of deposited matter.

In addition to these downward losses, there is a possibility of an upward loss or, at least, an upward redistribution. Over the sea, most of the salt particles are trapped beneath the temperature inversion which is generally present. Increased solar heating and turbulence over the land cause the inversion to break down, so that the salt is free to distribute itself throughout a much greater depth of air. This certainly occurs at times, and JUNGE and GUSTAFSON (1957) have recently argued that it may be the principal agency at work, at least in some regions. They showed that over the United States there is at first a rapid decrease in the concentration of airborne salt as one goes inland, but that it ceases after about 400 km. Over the interior of the continent the concentration seemed to be very nearly constant. Moreover, they produced some evidence to suggest that the total mass of salt in the column of air above 1 m^2 of the surface was much the same in the interior as over the sea, though spread of course through a much greater depth.

VOL.
1
958/9

The three mechanisms just considered—washout, direct deposition, and upward diffusion—appear to be the only *physical* ways in which gaseous or particulate matter can be removed from the air. Their relative importance no doubt varies greatly from place to place. In particular, upward diffusion is probably far less important in Scandinavia than in the trade-wind belt from which JUNGE and GUSTAFSON drew much of their evidence: for in Scandinavia, especially in winter, the inversion does not break down overland very readily. There remains a fourth possible mechanism—chemical combination at the surface. This certainly can be important in some cases: for example, plants extract from the air each day an amount of carbon dioxide equal to the whole amount in the lowest 500 m of the atmosphere, and it is conceivable that the rapid disappearance of chlorine is brought about in the same way.

This is a difficult matter. The decrease in the Cl : Na ratio, which is shown in Fig. 1 (c), is most obvious in the rainfall analyses, and the only discussions of it which have so far been published rely wholly on rainfall data. The explanation first put forward by CAUER (1949) and elaborated by ROSSBY and EGNER (1955) is that the salt particles in the air are partly oxidized, either by ozone or by sulphuric acid, so that chlorine is released. The residual sodium compound is then supposed to be washed out by rain, leaving the chlorine in the air. This would explain why the rain-water contains an excess of sodium: but, of course, it ought to follow that the air is left with an excess of chlorine—in other words, the ratio Cl : Na *in the air* ought

to increase inland. In fact, it decreases—not perhaps so strikingly as in the rain-water, but quite definitely. Somehow, therefore, the free chlorine is removed by some process other than washing out, and chemical combination at the surface seems the likeliest.

Junge and Gustafson (1957), however, have argued that there is no need to assume any decomposition of salt particles—that the decrease in the Cl : Na ratio can be explained by sodium compounds, other than the chloride, picked up by the air from the ground. But since there is no other possible source of the sodium except the sea, this is equivalent to saying that the soil collects salt from the air, extracts the chlorine, and returns part of the sodium as some other compound. A little consideration of the amounts which would have to be exchanged shows that the observed changes cannot easily be explained in this way. In particular, the Cl : Na ratio in rain-water, even on the windward coasts, often departs quite significantly from its sea-water value—ratios as low as 1·5 and as high as 2·1 are by no means uncommon—and these cannot have been brought about by a contribution from the ground. It seems certain, therefore, that some kind of decomposition of the airborne salt does take place, and that this is the fundamental cause of the variation of the Cl : Na ratio.

The topics which have here been discussed are those with which atmospheric chemistry has hitherto been most actively occupied. The principal one, which concerns the nature and origin of the inorganic salts in "clean" air, is of obvious importance in the context of atmospheric pollution, for it not only enters into the interpretation of all measurements made with pollution gauges but must in the end set the limit beyond which it is pointless to carry legislation against industrial pollution. The second main class of investigation relates to the mechanisms by which salts are removed from the air. This again has a direct bearing on pollution, and is much more easily studied by the methods of atmospheric chemistry. These, in effect, treat the sea as a source, so that the amount of material available for study is vastly greater than that from any industrial region. Moreover, measurements are made from a source-line—i.e. the coast—and this simplifies the problem by reducing it from a three-dimensional to a two-dimensional one.

Atmospheric chemistry, then, probably deserves more attention than it has hitherto received from students of pollution. It is equally true that the atmospheric chemists have so far paid scant attention to pollution, and the two sciences, which have so much in common, have remarkably little contact. The differences between them in terminology, in units, in the handling of data, and above all in outlook are astonishing. To take only one point, one could read most of the literature of atmospheric chemistry without encountering any specific mention of sulphur dioxide. There are of course clear historical reasons for this state of affairs. Atmospheric chemistry, the newer subject, has its roots in agriculture, and moreover, grew up in Scandinavia where pollution has never been a serious problem. But before long the atmospheric chemists will be forced to take pollution into account, for their network is spreading into industrial areas where it can no longer be ignored. There is indeed good reason to doubt whether it ought ever to be ignored, for Junge (1956) has recently produced evidence which strongly suggests that pollution, or at least material originating over land, remains suspended in the air during transits of thousands of miles and is a substantial part of the airborne material even over the oceans. Whether or not this is true, there is evidently a wide range of problems of equal importance to atmospheric

VO
1
1958

chemistry and to atmospheric pollution, and these can best be investigated by the two sciences working in collaboration.

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VOL.
1
958/9

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THE TECHNICAL PROVISIONS OF THE BRITISH CLEAN AIR ACT

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Abstract—The technical provisions relating to industry of this new legislation all come into force on 1 June 1958: the sections permitting the declaration of Smoke Control Areas in which domestic smoke is prohibited came into force on 31 December 1956. The main points of the technical regulations for the control of smoke, dust, grit and gases from industrial plants are quoted and discussed. Smoke from general industry is strictly limited in density and duration, and prior approval is required of dust arrestors and chimney heights for new factories. Administration of these regulations is by Local Authorities except that processes where there are special technical difficulties in preventing air pollution are placed under the supervision of the Alkali Inspectorate, who for 94 years have controlled many chemical works and whose duty is to ensure that best practicable means are used. No other country has such comprehensive legislation.

THE RELATION BETWEEN THE CLEAN AIR ACT AND PREVIOUS LEGISLATION

THE British Clean Air Act became law in July 1956 but most of its provisions did not have force until days " appointed " by the Minister of Housing and Local Government. The " appointed day " for some sections was 31 December 1956 and that for the remaining sections was 1 June 1958.

The prime purpose of this Act is to control and reduce emissions of smoke from both industrial and urban domestic premises and emissions of grit and dust from industrial premises in England, Wales and Scotland. Previously the Public Health Act, 1936, was the main law in force for the control of smoke in England and Wales, with a separate 1936 Act for London, and there were separate Acts for Scotland dating from 1897 to 1939. All these Acts constitute as statutory nuisances any industrial installations for the combustion of fuel which do not, so far as practicable, prevent the emission of smoke, but it was always a defence to show that the best practicable means had been adopted. Local Authorities, who were responsible for enforcement by means of abatement notices, found that the powers given were not strong enough, mainly for lack of definition of nuisance. Similarly, over 200 Local Authorities who made by-laws under the 1936 Act, making it an offence to discharge black smoke for a total of 2 min in any continuous period of 30 min, found that there was no effective definition of black smoke. No smoke is truly black. There were also nuisance provisions regarding any dust or other effluvia. Another weakness of these Public Health Acts was that they contained saving clauses whereby their provisions could not be applied if they obstructed or interfered with the working of mines or with several of the operations in iron and steel works. A useful summary of the position prior to 1956 is given in the Interim Report of the Government Committee on Air Pollution under the chairmanship of BEAVER (1953) which was appointed in July 1953 following the London smog of December 1952.

The Clean Air Act of 1956 follows closely the recommendations of the Final Report by Sir Hugh BEAVER's Committee (BEAVER, 1954). Although it gives some firm and

essential definitions, it is primarily an enabling Act enunciating general principles on which regulations with considerable technical detail may be made by the Minister of Housing and Local Government in respect of England and Wales, and by the Secretary of State for Scotland. These regulations, which are called Statutory Instruments, have the force of law from the date given on them provided they are not annulled by Parliament within 40 days of being laid before Parliament.* Frequently the Ministry issue at the same time explanatory circulars and memoranda to Local Authorities†—who administer the Act apart from those parts reserved for the Alkali Inspectorate (q.v.). Although there are always strong Parliamentary objections to the principle of " legislation by reference ", it will be appreciated from the review of these regulations given later that control will be more rapid and effective by the issue of regulations which can be readily changed in wording or technical effect to suit experience and progress in technology. There is also scope for experiment as between the English and Scottish regulations.

The Alkali etc. Works Regulation Act, 1906, which applies to England and Wales and with modifications to suit Scottish law, refers to pollution from certain chemical and industrial processes rather than from combustion. It replaced Acts under the same name dated 1881 and 1892. It is administered directly by the English and Scottish Alkali Inspectors appointed by the Ministry of Housing and Local Government, and Local Authorities in England and Wales may not, without the consent of the Minister, institute proceedings under the Public Health Acts if action can be taken under the Alkali Act. The Clean Air Act amends and extends the Alkali Act to give it effect in relation to smoke, grit and dust as it has effect in relation to noxious and offensive gases from works registered under the Alkali Act, but allows Local Authorities to obtain from the Minister an order to apply the Act to specified premises in respect of smoke, dust and grit emissions only. The Public Health (Smoke Abatement) Act 1926 and the Alkali etc. Works Regulation (Scotland) Act 1951 authorize the Minister to extend and amend the lists of Works scheduled under the 1906 Alkali Act, but not to revoke.

VOL. 1 958/9

TECHNICAL GROUPINGS UNDER THE CLEAN AIR ACT

Before discussion of the technical provisions of the Act, it is as well to consider the main groupings into which the Act is divided. In what follows, " Sections " mean sections of the Act and S.I. are Statutory Instruments issued under this and related Acts. References to the Ministry are to the Government Department at present known as the Ministry of Housing and Local Government which took over some of the responsibilities of the Ministry of Health in 1949.

(a) *Smoke from industry*

Sections 1–4, 16, 19–20: *S.I.* 1958 *No.* 498; *in force* 1 *June* 1958. These control smoke from steam raising and other simple furnaces in general industry, and including smoke from ships and railway locomotives.

The Fourth Schedule of the Act repeals the clauses in the Public Health Acts protecting mines, iron and steel works.

* Thus there were debates (HANSARD, 1958) in Parliament on 13 and 14 May on a prayer for annulment of Alkali Works Order S. I. 1958 No. 497, dated 24 March 1957. The motion was subsequently withdrawn.

† Since this paper was prepared, the Ministry has issued the following: *Clean Air Act Memorandum on Industrial Provisions S.O.* Code 75–59.

(b) *Grit and dust*

Sections 5–9; *in force* 1 *June* 1958. These control grit and dust from furnaces.

(c) *Chimneys*

Section 10; *in force* 31 *December* 1956. This secures examination of height of new chimneys to secure adequate dispersal of smoke, dust and gases.

It does not apply to public supply power stations, the chimneys for which are considered by the Ministry of Power.

(d) *Processes scheduled under the Alkali Act*

Section 17: *S.I.* 1958 *No.* 497; *in force* 31 *December* 1956 *and* 1 *June* 1958 *respectively*. The Act extends the Alkali Act to cover smoke, grit and dust as well as noxious and offensive gases, and now empowers the Minister to make Orders revoking any of the works scheduled under the Alkali Act. These Orders can only be made after a public enquiry at which it must be proved to the satisfaction of the Court of Enquiry, and against any opposition by Local Authorities and others, that the industrial processes for which registration is requested present special technical difficulties in respect of emissions of smoke, dust, grit and noxious gases. Following a public enquiry for England and Wales, S.I. 1958 No. 497 gives the list of works added to the list given in the Schedule to the Alkali Act of 1906. An abstract of the more important processes given in S.I. 497 and in the original Act is given in Appendix 1.

(e) *Smoke from houses: smoke control areas*

Sections 11–13; *in force* 31 *December* 1956. These sections provide for the declaration of " Smoke Control Areas " by Local Authorities subject to confirmation by the Minister who must hold a public enquiry if objections are raised. No smoke may be emitted in a Smoke Control Area except from defined premises and then only with limitations defined in the Order. The Areas may include industrial and commercial premises. The Act does not repeal those Local Authority Acts for the establishment of " Smokeless Zones " which are substantially similar to Smoke Control Areas.

VOL 1 1958

DEFINITIONS UNDER THE CLEAN AIR ACT

Although it is often tedious for the reader, it is almost always better to quote the actual words than to give an abstract of an Act of Parliament when important technical detail is concerned. In the following section of this paper, quotations from the Act are given in italics, together with the Section of the Act or the associated Statutory Instrument.

Smoke—34(1)—*Smoke includes soot, ash, grit and gritty particles emitted in smoke.*

Dark Smoke—34(2)—*Dark smoke means smoke which, if compared in the appropriate manner with a chart of the type known at the date of the passing of this Act as the Ringelmann Chart, would appear to be as dark as or darker than shade* 2 *on the chart.*

The Act also states in effect that a prosecution may be brought without there being an actual comparison of the smoke with a Ringelmann chart. A trained Smoke Inspector can judge whether a smoke is appreciably darker than Ringelmann 2.

Black smoke

S.I. 1958 No. 498 states that black smoke is as dark as or darker than shade 4 on the chart. This is the first time that black smoke has been legally defined in Britain. Nevertheless, there is no definition of black smoke in the Act and it is consequently possible to challenge in the Courts the introduction of this definition in a Statutory Instrument.

Determination of darkness of smoke

Fig. 1 shows the Ringelmann chart on a reduced scale. The black lines on the

charts numbered 1–4 obscure 20, 40, 60 and 80 per cent of the white paper. The chart must be held vertically with uniform illumination from the sky, close to the line of sight between the observer and the top of the chimney and at such a distance (about 50 ft) from the observer that the lines merge and each shade appears as a uniform grey. The reader should get the same impression by using Fig. 1 from a distance of 10 ft.

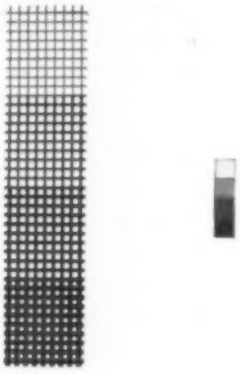

FIG. 1. The Ringelmann chart.

VOL.
1
958/9

The assessment of the darkness of smoke against a Ringelmann chart is purely subjective, i.e. it is liable to error due to the observer and to conditions of observation. Thus the shade of a smoke as viewed when it issues from a chimney arises from both transmitted and reflected light; hence the brightness and uniformity of the sky, the wind velocity and the diameter of the chimney can affect the observation. Since the Ringelmann chart measures shades of grey, it is not possible to assess with it the density of brown smoke or of a light coloured plume of carbon-free dust. Nevertheless, under good conditions, trained observers can agree on the shade of ordinary carbonaceous smoke arising from bad combustion of coal to about a quarter of a Ringelmann shade.

Measurements made by the FUEL RESEARCH STATION (1955) for a British Standards Committee on Smoke Density Meters have shown that the wider the chimney mouth the darker is the appearance of a smoke of the same optical density, conditions of sky and wind velocity being constant.* The measurements so far made indicated, for example, that smoke appearing as Ringelmann 2 when discharged from a chimney mouth of 4 ft diameter would appear as Ringelmann 3 if discharged from a chimney of 8 ft diameter. Although this must not be taken as precise, it does indicate that, under the Act, operators of large plants must produce smoke of lower optical density, and therefore lower suspended soot content, than operators of small plants when both are producing smoke of borderline density just below Ringelmann 2. Evasions of this requirement by use of many small chimneys can be prevented by section 10 (on approval of plans for new chimneys).

* Smoke Density Indicators and Recorders, Appendix B of British Standard 2811: 1957.

The British Standards Institution has recently produced a specification B.S. 2742 on " The Use of the Ringelmann Chart " which should be studied by all those who use the chart. Concurrently they have also issued a British Standard Ringelmann Chart B.S. 2742C. It was found by those responsible for the preparation of this standard chart that the commercially printed charts, including those produced by the U.S. Bureau of Mines and the smaller 4 in. chart of Charles Griffin & Co. Ltd., London referred to in the Beaver Report, are printed on paper with a luminance factor of about 80 per cent with ink of luminance factor of about 5 per cent. The British Standard Chart reproduces the same shades of grey. It is, however, printed on Bristol board instead of semi-translucent paper which could be affected by the colour of the mount to which the chart is attached, and there is a strict printing specification for the dimensions of the grid lines.

As an assistant is required to hold any of the three above mentioned charts over 50 ft from the observer, much interest has been aroused in the announcement in B.S. 2742 that an attempt is being made to produce a miniature smoke-chart which can be used by a single observer; the commercially produced small charts, useful for rough work, are not of the consistency necessary for measurements which may have a legal significance. What is badly needed is an instrument which will measure the Ringelmann shade of a smoke without observational error and from a point outside the chimney, and Section 34(2) empowers the Minister to prescribe, by regulation, such a method of measurement. No instrument so far produced has met the necessary technical requirements.

Practicable—34(1)—*Practicable means reasonably practicable having regard, amongst other things, to local conditions and circumstances, to the financial implications and to the current state of technical knowledge.*

Practicable Means—34(1)—*Practicable means includes the provision and maintenance of plant and the proper use thereof.*

The Alkali Act 1906, Section 27, uses wording having similar effect (see later), though it and the Public Health Act 1936 omit reference to the current state of technical knowledge—an important clarification.

Fireplace—34(1)—*Fireplace includes any furnace, grate or stove, whether open or closed.*

Oven—34(1)—*Oven includes any form of retort or container used to subject solid fuel to any process involving the application of heat.*

Industrial Plant—34(1)—*Industrial plant includes any still, melting pot or other plant used for any industrial or trade purposes, and also any incinerator used for or in connexion with any such purposes.*

Chimney—34(1)—*Chimney includes structures and openings of any kind from or through which smoke or (where the reference is to the chimney serving an oven) grit or dust may be emitted, and references to a chimney of a building include references to a chimney which serves the whole or a part of a building but is structurally separate therefrom.*

Furnaces

No definition is given of furnace, but the following are important interpretations of the word " furnaces ":

S.I. 1958, No. 498—II(3)—*Where a single boiler or unit of industrial plant is fired by more than one furnace discharging to the same chimney those furnaces shall, for the purposes of these regulations, be deemed to be one furnace.*

VOL 1 1958

This means that in the Dark Smoke Regulations referred to later, a shell boiler with several furnace tubes is to count as one furnace and not several furnaces. The definition is to be read in conjunction with S.I. 1958, No. 498, which gives the permitted emissions of dark smoke during sootblowing and attention to fires.

34(7)—The following definition is in respect of the sections of the Act dealing with grit and dust emission from furnaces:

Any furnaces which are in the occupation of the same person and are served by a single chimney shall, for the purposes of Sections 6–8 *of this Act, be taken to be one furnace.*

34(1)—*Authorized Fuel means a fuel declared by regulations of the Minister to be an authorized fuel for the purposes of this Act.* (This definition refers to sections of the Act dealing with Smoke Control Areas.)

S.I. 1957, No. 541—3; S.I. 1957, No. 544 (S. 27)—3 (for Scotland)—*Fireplaces specially designed or adapted for combustion of liquid fuel shall, provided that they are so installed, maintained and operated as to minimize the emission of smoke, be exempted from the provision of Section* 11 *of the Clean Air Act*, 1956 (*which relates to Smoke Control Areas*).

REGULATIONS ON SMOKE EMISSION

Permitted periods of dark and black smoke under Section 1

Under Section 1 (1) of the Act it is an offence to emit dark smoke from a chimney except that:

Section 1(2)—*emissions of smoke from any chimney lasting for not longer than such periods as may be specified by the Minister by regulations shall, in such classes of case and subject to such limitations as may be so specified, be left out of account for the purposes of this section.*

Regulations under Section 1(2)—*S.I.* 1958, *No.* 498

This gives a permitted period for dark smoke emissions. Longer periods of time are allowed when the plant is equipped with sootblowers, and the total permitted period of emission in any period of 8 hr increases with the number of furnaces discharging to the chimney up to a limit of four furnaces. Units with more than one furnace, e.g. Lancashire boilers, shall be deemed to be one furnace.

From their form, it is probable that these regulations have been framed primarily

TABLE 1. PERMITTED PERIODS OF DARK AND BLACK SMOKE

No. of furnaces per chimney	Permitted minutes dark smoke in aggregate in any period of 8 hr		Continuous emission of dark smoke other than that arising from sootblowing	Maximum emission black smoke in aggregate in 30 min
	No sootblowers	With sootblowing	(min)	(min)
1	10	14	4	2
2	18	25	4	2
3	24	34	4	2
4 and more	29	41	4	2

to cover emission of smoke from boilers, bearing in mind that the Beaver Report implied that inexpert firing of boilers and lack of suitable mechanical firing equipment for the fuel burned were responsible for the general industrial smoke over towns. The Beaver Report stated that there are about 40,000 handfired industrial boilers in the country, whilst the report of the National Industrial Fuel Efficiency Service (NIFES) for the year ending 31 March 1957 estimated that there were 18,000 Lancashire boilers in regular use.

A criticism that can be levelled against this regulation is that it does not cover as many general cases as those advising on the technical framing of the Act probably intended. Thus there will probably be great difficulty in conforming with the regulation in the following types of plant:

(a) Shell boilers, even with mechanical stokers, burning highly caking coal because this type is the industrial coal indigenous to the district. Frequent slicing of fires is necessary with such coals.

(b) Shell boilers which are banked overnight and from which full steam output is required immediately on start of work in the morning. Lighting up from cold is covered in Section 1(a), q.v.

(c) Process furnaces requiring long gentle flames. In these smoke would be reduced by using excess air but there would then be substantial loss in thermal efficiency.

(d) A few process furnaces where difficulties exist with modern plant in preventing smoke emission but not sufficiently to secure registration under the Alkali Act as having special technical difficulties.

(e) Works incinerators burning a great variety of substances. (Chemical works incinerators burning specified products are included under the Alkali Act—see Appendix.)

Large water-tube boiler installations are unlikely to experience any difficulty in conforming and might well have been asked to do better than shell boilers since measurements of the smoke emission from a few modern and well run plants with travelling grates have shown that average emissions of dark smoke in excess of 6 min per shift of 8 hr per boiler can be achieved with boilers within the size range 30,000–50,000 lb/hr.*

To aid administration of S.I. 498, Local Authorities have powers under the Public Health Act 1936, Section 287, to enter or inspect premises, e.g. to see records of soot-blowing times. Factory managements should therefore make arrangements for appropriate records to be made by their boiler operators and for the records to be kept.

Temporary relaxations from Section 1

As recommended in the Beaver Report, Section 2 states that for not more than 7 years from the passing of the Act (i.e. until July 1963) it will be a defence under Section 1 to prove that the contravention was due to the nature of the equipment and that it had not been practicable to alter it to be fully used for the purpose for which it was intended without contravening Section 1. Section 2(2) states that Local Authorities may issue annual certificates to this effect. The onus is, however, on the factory owner, and Section 2 must not be regarded as a temporary licence until 1963 to make smoke by careless operation. It is probable, therefore, that by 1963 Local Authorities will expect hand firing of boilers to be discontinued, and all sprinkler or other forms

* *Measurements of Smoke Emission from Industrial Boilers—*1. *Medium Capacity Coal-fired Water-tube Boilers with Travelling Grates.* British Standard 2978: 1958.

VOL 1 1958

of stoker to be replaced if there is excessive smoke from them with local coals. Many small factories will undoubtedly change over to oil firing as a result.

Defences under Section 1

Section 1(3) of the Act states that it will be a defence to prove either:

(a) *That the contravention complained of was solely due to the lighting up of a furnace which was cold and that all practicable steps had been taken to prevent or minimize the emission of dark smoke; or*

(b) *That the contravention complained of was solely due to some failure of a furnace or of apparatus used in connexion with a furnace, that the failure could not reasonably have been foreseen, or, if foreseen, could not reasonably have been provided against, and that the contravention could not reasonably have been prevented by action taken after the failure occurred; or*

(c) *That the contravention complained of was solely due to the use of unsuitable fuel, that suitable fuel was unobtainable, that the least unsuitable fuel which was available was used and that all practicable steps had been taken to prevent or minimize the emission of dark smoke as the result of the use thereof; or*

(d) *That the contravention complained of was due to the combination of two or more of the causes specified in paragraphs (a) to (c) of this sub-section and that the other conditions specified in those paragraphs are satisfied in relation to those causes respectively.*

The word " solely " in the above sections places an important limitation on these defences except for the permissible combinations of (a) to (c). It will be necessary for a defendant to prove that there are no other causes.

VOL.
1
958/9

It remains to be seen whether Local Authorities will consider that the best practicable means for lighting up cold furnaces burning pulverized fuel or heavy oil includes use of light oil starting-up burners and whether coal gas, if available, should be used for assisting rapid production of a steady fire on a cold shell boiler. Only actions in the courts will decide whether the law on the defence of unsuitable fuel is drawn sufficiently tightly to prevent abuse without at the same time being unduly onerous in cases of genuine difficulty. Evidence from the marketing department of the National Coal Board will play a considerable part in deciding the issues.

Railway engines (Section 19)

Section 1 is to apply to railway engines but is tempered by Section 19 to the effect that owners must use any practicable means there may be to minimize smoke. Grit and dust emissions are expressly excluded.

Although steam induced secondary air devices for works locos have been described (Brooks and Calvert, 1957), it is probable that most owners will be driven to replace coal fired engines by diesels by 1963, and a good financial case can be made for so doing. Main line locomotives will mostly have been replaced by diesel or electric locomotives by 1963 and the Act will put Local Authorities in such a strong position that coal fired engines will cease to be used in works. Cranes running on rails will probably be counted as railway engines to which Section 19 applies.

Ships (Section 20)

Sections 1 and 2 apply to ships in inland waters and to seagoing ships within docks, estuaries, etc. in the areas where financial charges can be made for services other than

lights and pilotage. S.I. 1958 No. 498 does not, however, apply: regulations for ships given in S.I. 1958 No. 878 were only laid before Parliament on 29 May. The periods for which dark smoke is permitted are far longer than those for land boilers and vary both with the type of boiler furnace and vessel duty. They are:

Ships furnace	Maximum permitted emission of dark smoke
Forced-draught oil-fired (or oil engine)	10 min in any 2 hr 4 min continuous except when sootblowing*
Natural-draught oil-fired	10 min in any hr 4 min continuous except when sootblowing*
Coal-fired	
Vessel under way	20 min in any hr
Vessel not under way (except in special cases below)	10 min in any hr
Vessels with n-d oil or coal furnaces in special cases	20 min in any hr 10 min continuous except when sootblowing*
(a) With short funnels for navigating Manchester Ship Canal (b) Tugs preparing to get under way or supplying power to other vessels. (c) Vessels using main power for dredging, pumping etc.	* Sootblowing refers in all cases to water-tube boilers.

Emissions from any other source may not exceed an aggregate of 5 min in any hr. In no case may black smoke be emitted for more than an aggregate of 3 min in any ½ hr.

Requirements that new furnaces shall be smokeless (*Section* 3)

Every new furnace ordered after 31 December 1956 shall, so far as practicable, be capable of being operated without emitting smoke when burning fuel of the type for which the furnace was designed. Notice of the intention to install any new furnace must be given to the Local Authority. If plans for the furnace are in addition sent to and approved by the Local Authority, there can be no prosecution for installing a furnace which does not comply with this section. Ministry of Housing and Local Government Circular No. 658, 7 February 1958, contains an Appendix on " Notes for guidance of Local Authorities in giving approval to new furnaces ".

The purpose of this " prior approval " is to exert some supervision on operators who may build their own furnaces instead of purchasing tried designs, and to check that any proposed furnace is suitable for the fuel supplies expected to be available. It is not obligatory to obtain prior approval. Compliance with this section is not, be it noted, a defence if the new furnace emits, when in service, more smoke than is permitted under S.I. 1958, No. 498.

Smoke density meters (*Section* 4)

The Minister may make regulations requiring installation of indicating or recording smoke density meters on any type of specified furnace, using and maintaining the apparatus in pursuance of the regulations, and making available to the Local Authority any results recorded by the apparatus; but he does not propose to make any regulations just yet. There is the difficulty that the heaviest smoke producers are small factories in which there would be the greatest difficulty in keeping the meters in commission and correctly calibrated. The Ministry is more likely first to issue regulations requiring the installation of simple smoke viewers in small plants. For the time being further experience is necessary with voluntarily installed instruments, and it advises Local Authorities to encourage their use. Smoke meters are highly desirable adjuncts to all plants where faulty operation leads to dark smoke, as they enable boiler operators to see when the smoke is approaching the legally permitted limit.

Relevant British Standards specifications are:

2740:1956—*Simple Smoke Alarms and Alarm Metering Devices*
2811:1957—*Smoke Density Indicators and Recorders*
2741:1957—*Recommendations for Construction of Simple Smoke Viewers.*

Since 2741 was published the Fuel Research Station has developed (HILL, 1958) an improved form of smoke viewer element using electric fire elements as a source of light instead of an electric filament lamp. The heat element is in the flue gas and is not protected by a window as is the case with the filament lamp; there is thus the advantage that only the viewing window requires periodical cleaning and this is readily accessible.

VOL.
1
58/9

REGULATIONS ON DUST EMISSION

Requirements that grit and dust from old and new furnaces shall be minimized (*Section* 5)

Section 5 contains the general requirement that " any practicable means there may be " shall be used to minimize the emission of grit and dust from any chimney.

The Section applies even to domestic furnaces having a maximum heating capacity greater than 55,000 B.t.u./hr (at 50 per cent efficiency, this means any plant burning more than 10 lb/hr of coke or coal). It will remain for the Courts to decide the meaning of " any practicable means ". For small plants it may be decided that a simple settling chamber, or even a method of operating the fire to minimize grit and dust emission, is sufficient. As the Section came into force on 1 June, Local Authorities are advised by the Ministry of Housing that they will have to allow time for industry to install grit and dust arrestors on existing plant to comply with Section 5. It would certainly seem that grit arrestors must be installed on existing shell boilers using sprinkler stokers. Undoubtedly pressure will be brought to bear by Local Authorities on factories around which there is complaint of grit and dust emission. The Ministry is advising that attention should first be paid to old plants of type and size given in Section 6.

Requirements that new furnaces shall be fitted with grit and dust arrestors (*Section* 6)

Prior approval must be obtained from the Local Authority of the dust and grit arrestors installed on new plant burning (a) pulverized fuel (b) over 1 ton/hr of solid fuel or solid waste. An appeal may be made to the Ministry if there is dissatisfaction

with the ruling of the Local Authority. Section 6 also states that plant must be properly maintained and used.

There should be little argument about the need for the effective removal of grit but difficulties arise with larger plants in respect of residual fine dust. As the Beaver Report states (paragraph 36):

> " the important factors are the weight of dust discharged, the size of the particles and whether the chimney is of sufficient height to disperse the residual dust adequately. It is, in effect, difficult to lay down maximum tolerable limits for grit and dust emissions and they must be related to the size of the plant."

The necessity for considering height of chimney and weight and size of dust escape is discussed in the heading " Chimneys ".

Dust nuisances to which Sections 5–9 do not apply (e.g. certain open air processes) can be dealt with under Part III of Public Health Act 1936, particularly Section 92(1)(d).

Measurement of grit and dust (*Sections* 7 *and* 8)

The Minister may make regulations to cover the making and recording of measurements, from time to time, of grit and dust emission from all pulverized fuel plants and all plants burning more than 1 ton/hr solid fuel or solid waste. The distinction between grit and dust given by the Beaver Committee is that dust consists of particles which will pass a 200 BS test sieve, aperture size 76 μ.* The regulations may make different provisions for different classes of furnace.

The Local Authority may also serve notice in writing requiring relevant information on the furnaces and the fuel burnt in them.

British Standard 893 on the testing of dust extraction plant at power stations describes a lengthy and complicated procedure which is only suitable for acceptance tests and occasional checks on existing plants. Following a recommendation of the Beaver Committee, British Standards Institution is preparing a specification for simpler methods of determining the emission of grit and dust. Methods which give an accuracy of ± 25 per cent should be adequate for most purposes. From the delay it is evident that difficulties are being experienced in the preparation of recommended methods which can be generally applied without too many exceptions arising from the layout of the plant at which measurements are to be made. A description of recent equipment developed by the British Coal Utilisation Research Association together with references to other modern apparatus has recently been published (HAWKSLEY *et al.*, 1958; STAIRMAND, 1951). Simple instruments, similar to smoke meters, are urgently required for indicating appreciable changes in dust and grit emission.

EFFECTS OF GASES AND DUST AT GROUND LEVEL

Heights of chimneys (*Section* 10)

Plans for new chimneys for discharge of smoke, grit, dust or gases (other than plans for chimneys on residences, shops and offices or power stations) are to be rejected by the Local Authority unless they are satisfied that the height of the chimney will be sufficient to prevent, so far as practicable, the smoke, grit, dust or gases from becoming prejudicial to health or a nuisance having regard to: (a) the purpose of the chimney; (b) the position and description of buildings near thereto; (c) the levels of the neigh-

* This definition now appears in British Standard 2955: 1958, *Glossary of Terms Relating to Powders*.

bouring ground; and (d) any other matters requiring consideration in the circumstances. Reasons must be given for rejection.

This is the only Section in which reference is made to the discharge of gases. Excluding chemical and similar manufacturing processes, the gas to which reference is made is sulphur dioxide in flue gases, a subject which was discussed at some length in the Beaver Report.

The only advice (MINISTRY of HOUSING and LOCAL GOVERNMENT, 1956a) which the Ministry has so far given to Local Authorities on the technical considerations governing the heights of chimneys is a reference to Appendix VI of the Beaver Report which indicates the need in the first place to check that the chimney is sufficiently high above surrounding buildings or land obstacles to avoid the carrying to ground of the flue gases by down-draughts of air currents caused by the obstacles. When the buildings are large, the chimney should preferably be at least $2\frac{1}{2}$ times their height with a minimum of 120 ft but discretion must be used for smaller plants. Down-wash of flue gases along the side of the chimney, which is evidenced by blackening of the tops of chimneys and which lowers the effective height of the chimney, should be avoided when there is an induced draught fan by maintaining the velocity of emission above 40 ft/sec. The discharge from as many furnaces as possible should be led to a single chimney as the larger the mass or volume of a discharge at any given temperature, the slower the rate of cooling of the plume by admixture with air and therefore the greater the buoyancy. The thermal rise from large chimney discharges can in fact amount to several hundred feet in low winds and this is in effect a substantial addition to the effective height of the chimney.

VOL.
1
58/9

The discharge from a chimney rises due to buoyancy and then generally spreads out into the shape of a cone which, under average wind conditions, has a half angle of 5–10°. The result is that part of the "smoke", greatly diluted, will reach the ground at a point, with average winds, some 8 to 10 times the effective height of the chimney. Dust which is less than 20 μ Stokes' diameter will travel with the gases, and coarser material will fall spread in a band closer to the base of the chimney according to the size of the particles. To determine whether a proposed chimney is likely to be sufficiently high to avoid nuisance, it is therefore desirable to calculate the worst conditions likely to occur over a small area at ground level (or upper window level of residences and possibly trees) and to have some knowledge of the threshold limits of pollution below which appreciable nuisance will not arise. Calculations can now be made of ground level conditions by means of formulae derived by SUTTON and by BOSANQUET, or by an empirical formula proposed by the U.S. Atomic Energy Commission, Oak Ridge (see Appendix VI of the Beaver Report). A general introduction to the whole subject is given by HAWKINS and NONHEBEL (HAWKINS and NONHEBEL, 1955; SUTTON, 1947; BOSANQUET, 1957; BOSANQUET *et al.*, 1950; BEST, 1957).

Bearing in mind the continual variations in the micro-meteorology of a district, it is satisfactory that limited tests of these formulae indicate that they can predict worst ground conditions within a factor of 2 when there is not an atmospheric inversion. They should be used therefore in place of guesses on the suitable height for a chimney. They show, for example, that whereas high chimneys are always advantageous for dispersion of gases, cases can arise where it is better to use a short chimney to ensure that grit falls within a factory area instead of being thrown by a high chimney on to a group of houses.

It is hoped that the Ministry will, in due course, give guidance on desirable maximum concentrations of SO_2 or solids deposition rates from proposed new chimneys. Once dark smoke arising from bad combustion has been effectively diminished, the cost of reduction in amenity arising from SO_2 and dust must be balanced within reason against the cost of reducing their effects. Recent measurements in London give concentrations of SO_2 of about 15 p.p.h.m.*, whilst the average of maximum concentrations at observing stations during the 1952 London smog was 60 p.p.h.m. In Germany STRATMANN (1956) has stated that leaves of trees are damaged by intermittent exposure to concentrations in excess of 50 p.p.h.m. SO_2. Taking into account the uncertainties of the above mentioned calculations, it would appear that the height of each new chimney should be that which gives a calculated maximum point concentration below 25 p.p.h.m.; calculated concentrations from large power stations with 300 ft chimneys are well below this (HAWKINS and NONHEBEL, 1955).

The tolerable dust deposition rates can also be assessed from a study of measurements made by Local Authorities under the auspices of the Department of Scientific and Industrial Research. Average figures are given in Table 2 (WILKINS, 1957).

TABLE 2. DEPOSITS OF SOLID MATTER IN BRITAIN

Type of district	Rate of solid matter deposition (tons/mile² per year†)
Rural	50
Cities and light industrial	200–400
Heavy industrial	500–2000

† Multiply by 39 to convert to g/100 m² or by 1·16 to convert to oz/100 yd². The figures refer to these small areas and not to a square mile.

Since dust free from tar is a nuisance rather than detrimental to health (except when the particles are smaller than 10 μ) and, since we cannot expect to have rural conditions in our towns, it would be reasonable to expect the maximum contributions at any point from the chimneys of a new installation not to add more to the existing rate of dust deposition than 50 tons/mile² per year in areas of light industry and 150 in areas of heavy industry. The above suggestions, which represent a reduction of about the 80 per cent recommended in the Beaver Report, are undoubtedly controversial but are given in the hope that the Ministry will put forward reasoned guidance to Local Authorities based on a careful study of available information. Even then, any recommendations need to be reviewed every 5 years in the light of experience gained from suitably arranged measurements.

The Ministry have not given any guidance to Planning Authorities who often dislike high chimneys because they obtrude on the sky-line.

Smoke nuisances (*Section* 16)

If it is a nuisance to the inhabitants of a neighbourhood, Local Authorities may issue abatement notices in respect of any smoke, whether from a chimney or not, except when it comes from a private dwelling or is dark smoke from a chimney. The

* Parts per hundred million.

VOL 1 1958

section covers open fires for burning rubbish, coloured smoke from chimneys the density of which cannot be measured by the Ringelmann chart and even ordinary smoke lighter than Ringelmann No. 2. It therefore catches all cases not coming under Section 1 or under Smoke Control Areas. If the abatement notice has no effect, a " nuisance order " may be obtained in a magistrate's court under the procedure of Part III of the Public Health Act. A novel addition to the latter is that a " nuisance order " may be obtained in respect of a likely recurrence of an incident and the court may order execution of necessary works. Only in the case of smoke from a chimney is it a defence to prove that best practicable means have been taken. The Section does not apply to grit and dust emissions: those from furnaces are covered by Sections 5 and 6 and other dust and grit nuisances are covered by Section 92 of the Public Health Act 1936.

Colliery spoilbanks (*Section* 18)

Best practicable means are to be taken to prevent or minimize smoke and fumes from deposits of refuse from mines or quarries. The section does not apply to tips not in active use at the date of the passing of the Act and not under the control of the owner of the mine or quarry, but control can still be exercised through Section 16 or the statutory nuisance procedure of the Public Health Act.

Research and investigation (*Section* 21)

To enable investigations or research on problems of air pollution to be carried out, Local Authorities may exempt applicants wholly or in part from proceedings under Sections 1, 3, 5, 6, 7, 11, 16 and 19. It is not clear why investigations on vessels are excluded. This exemption is most necessary for those undertaking work on the improvement of equipment, particularly as full-scale tests of new designs and modifications are the final test.

VOL. 1 58/9

PROCESSES SCHEDULED UNDER THE ALKALI ACT

(*Section* 17)

All processes (see Appendix) registered under the Alkali Act must now take the best practicable means for preventing the emission of noxious or offensive gases, smoke, grit and dust. Section 27 of the Alkali Act states that these means have reference not only to *the provision and efficient maintenance of appliances adequate for preventing such escape, but also to the manner in which such appliances are used and to the proper supervision by the owner of any operation in which such gases are evolved.* Presumably registration, which has to be renewed annually, can be refused if pollution-collecting appliances are not considered to have the required efficiency. The Inspector, it will be noted, can also require the process itself to be operated in such a way as to minimize production of pollutants and he can require provision of necessary instruments and employment of trained operators. Only that part of a process plant which leads to air pollution need be registered.

Proceedings for emission of smoke etc. under Sections 1, 5 and 16 of the Clean Air Act can, however, also be taken by Local Authorities with the consent of the Minister, but an additional defence is that best practicable means have been taken. In addition the Minister has power to transfer administration of part of any premises registered under the Alkali Act from the Alkali Inspectorate to a Local Authority but only in

respect of smoke, dust and grit, not gases. The Local Authority will have to satisfy the Minister that it has the appropriate staff for this duty.

The powers behind the Alkali Inspectorate are immense though they have always been used to persuade factory owners to improve processes, and prosecutions have been extremely few. The wide range of problems considered by the Inspectorate and accounts of their difficulties and some solutions are given in their Annual Reports, of which the ninety-fourth, that for 1957, has recently been issued.

The reason for placing the processes listed in the Appendix under the supervision of the Inspectorates* is that they all present problems of special difficulty and that constant general control by an experienced body of men with special technical qualifications under a central control with access to information from anywhere in the world is the only method whereby design and operational methods of plant can be kept up to date. If the original design of a large pollution-prevention plant, which might cost over £1 million for a large power station, turns out in practice to be poor, the improvements that can be made at reasonable cost and dislocation to the operation of the process plant are usually only marginal: original design is therefore all important.

The Act empowers the Minister to remove from the list of scheduled processes any for which the special supervision by the Alkali Inspectorate is no longer considered necessary.

Since the English Alkali Inspectorate will only have a strength of about 28 when enlarged to meet the requirements of the Act (HANSARD, 1958), day-to-day observation of polluting chimneys will not be possible. Local Authorities can, however, report to the District Alkali Inspector any cases where their own observations indicate deterioration in emissions. Close co-operation is a necessary condition for supervisions. Such co-operation has, however, always existed and the Annual Reports of the English and Scottish Alkali Inspectors regularly contain sections on unregistered works upon which the Inspectorates have been asked for advice.

Not all the processes suggested by Industry in the enquiry held in 1957 were accepted for registration, and it has thereby been indicated that requests for registration on grounds of special technical difficulty are not automatically granted. The principal rejections were of some metallurgical operations, mostly in the iron industry. The Order S.I. 1958 No. 497 will apply to about 2000 works out of a total of about 30,000 throughout the country which produce smoke. These 2000 works used last year 110 million tons of coal (41 million in power stations), and $2\frac{1}{2}$ million tons of fuel oil. (HANSARD).

Smoke control areas (*Sections* 11–15)

Section 11 states that "Any Local Authority may, by order confirmed by the Minister, declare the whole of the district of the Local Authority or any part thereof to be a smoke control area. Subject to any exemptions and limitations for the time being in force under this section, if, on any day, smoke is emitted from a chimney of any building within a smoke control area, the occupier of that building shall be guilty of an offence." As in the Smokeless Zones operated by some Local Authorities, it is a defence to prove that the emission of smoke was caused by an authorized fuel.

* There is one Inspectorate for England and Wales and a separate Inspectorate for Scotland. There are minor differences in legal procedure in Scotland.

Although these sections of the Act are primarily intended to cover residential areas, factories may be included in Smoke Control Areas. Specified buildings in them may, however, be exempted in the order from being smokeless, in which case the general law of Section 1 applies, or they may be allowed to make defined emissions of smoke. All proposed orders must be duly notified, and if objections are raised, the Minister must cause a local enquiry to be held before confirming the order with or without modifications. No order can come into force until at least 6 months after confirmation.

Industry will therefore be affected by these Sections of the Act, especially light industries near residential areas. The rate at which Smoke Control Areas will be declared depends both on the pressure of public opinion in Local Government Areas and on the supply of smokeless fuel locally available for houses. The Ministry has advised (MINISTRY of HOUSING and LOCAL GOVERNMENT, 1956b) that local industry should not be asked to use smokeless fuel such as coke where use of *suitable* coke in houses would do more to reduce smoke, but it has also suggested that some reduction in the frequency of smoke emissions from coal-fired plant could be obtained by re-equipment with mechanical stokers designed for minimum smoke emission. Following a recommendation in paragraph 97 of the Beaver Committee, a British Standards Committee has been making measurements of the duration of emissions of dark smoke made in practice and without special supervision from boilers equipped with well designed stokers and combustion chambers and operated under good commercial conditions. The first report* on industrial water-tube boilers concludes that average emissions of dark smoke in cases of 6 min per shift of 8 hr per boiler can normally be avoided in water-tube boilers with travelling grates within the size range 30,000 to 50,000 lb/hr. Measurements on Lancashire, Economic and Vertical type shell boilers are proceeding. Local Authorities might ask for smoke emission from factories in Smoke Control Areas to be of similar standard.

Alternatively, use of oil firing in smoke control areas is now permitted in a special Order† issued under the Act. Details have been given above under " Definitions ".

Clean air councils (*Section* 23)

Separate Councils have been appointed‡ for Scotland and for England and Wales to review progress made in abating air pollution and for the purpose of obtaining the advice of those having special knowledge, experience or responsibility on the subject. The Councils, who have 22 members for Scotland and 32 for England and Wales, include 13 and 18 (including one trade unionist) representatives of general and nationalized industry respectively; other representatives are drawn from the staff and elected members of Local Authorities.

REVIEW

The Clean Air Act has followed closely the recommendations for legislation made by the Beaver Committee. Previously designers of equipment for new factories had

* British Standard 2978: 1958, loc. cit.

† *The Smoke Control Areas* (Exempted Fireplaces) Order, S.I. 1957, No. 541. *The Smoke Control Areas* (Exempted Fireplaces) (Scotland) Order, S.I. 1957, No. 544 (S. 27).

‡ *The Clean Air Council Order*, S.I. 1957, No. 766. *The Clean Air Council* (Scotland) *Order*, S.I. 1957, No. 1944 (S. 96).

VOL. 1 58/9

no specifications for emissions to which they should work. Now smoke from general industry is strictly limited in terms of density and duration and prior approval of apparatus for grit and dust collection is required. No other country has such comprehensive legislation covering all areas uniformly; even the regulations for the locally declared Smoke Control Areas are controlled by the Act. Nevertheless, the success of the Act in achieving massive reduction of smoke from the smoky areas of Britain will depend on co-operation by industrialists led by effective administration on the part of Local Authorities. Both are influenced by public opinion in their areas. There have been complaints against the defence of unsuitable fuel, and it remains to be seen how the Courts interpret the Act. The administration of most legislation has, in fact, to be judged by the case law which is ultimately built up, and the real success of the Act will be shown by reduction of industrial and domestic smoke without frequent recourse to the Courts. Fears have also been expressed by Local Authorities that the absence of day-to-day control of processes of special technical difficulty scheduled under the Alkali Act will result in heavier emissions of pollutants than necessary. On the other hand, experience with noxious gaseous emissions indicates that this is not so, once the best practicable means are established in terms of equipment and its operation, but it will obviously take some years for the Alkali Inspectorate to secure the improvements to existing plant which they consider necessary.

It may therefore be concluded that the Act will, in the course of years, secure such substantial diminution of industrial smoke that there will be a general demand by the population for reduction of domestic smoke through the medium of Smoke Control Areas. The general purpose of the Act is to secure steady improvement as technical knowledge increases on means for reducing air pollution, but it must be remembered that complete prevention of air pollution in any industrial country cannot be achieved. The Beaver Committee said: " Real improvement can be secured only by a continuous programme urgently and consistently carried out over a number of years. The objective of our recommendations is that by the end of 10 to 15 years the total smoke in all heavily populated areas would be reduced by something of the order of 80 per cent. This would mean a degree of freedom from air pollution which many parts of the country have not known for more than a century."

VO
1
1958

APPENDIX

The eleven processes registered under the Alkali Act from 1 June 1958

The following is abstracted from S.I. 1958, No. 497, to which reference should be made for definitions. The numbers are those added to the Second Schedule of the 1906 Act. The order is actually made under the Public Health (Smoke Abatement Act), 1926.

30. Certain Iron and Steel Works processes, including sintering plants for ore, blast furnaces, Bessemer, open hearth and electric arc furnaces, works in which oxygen is used for refining iron or finishing steel.

31. Copper Works in which (a) molten copper or its alloys is deoxygenated with wood, (b) copper is cast in moulds dressed with oil or grease.

32. Aluminium Works for recovery of aluminium by certain processes.

33. Electricity Works (a) for public supply (b) industrial power stations where the aggregate maximum continuous rating of the boilers exceeds 450,000 lb/hr (equivalent to the combustion of about 20 tons/hr coal).

34. Producer Gas Works in which the gas is made from coal.

35. Gas and Coke Works including coke oven works, water gas plants and plants in which gas is made from coal or oil or such gas is purified.

36. Ceramic Works including (a) works for pottery works using intermittent kilns fired by coal or oil (b) works where heavy clay or refractory goods are fired by coal or oil in intermittent kilns, continuous grate-fired kilns or made-in kilns in which a reducing atmosphere is essential (this includes blue brick manufacture).
37. Lime Works in which limestone is burnt using coal.
38. Sulphate Reduction Works—for production of sulphides.
39. Caustic Soda Works where concentrated or fused caustic soda is produced in coal-fired vessels.
40. Chemical Incineration Works in which there are burned wastes produced during the manufacture of materials for the fabrication of plastics and fibres.

The further gases added to the list

The First Schedule of S.I. 1958, No. 497, adds the following to the previous list of noxious and offensive gases—compounds of ammonia, acetylene, fumes containing iron, aluminium and chlorine or their compounds.

Fluorine emissions from steel and ceramic works will be covered by the Second Schedule above mentioned.

The original list of registered processes

The original list in the 1906 Act with subsequent addition is too long for inclusion here but the following are of particular interest:

(a) Cement Production Works.
(b) Smelting Works in which sulphide ores are treated (including lead and zinc works).
(c) Sulphuric Acid Works—both chamber and contact processes.
(d) Nitric Acid Works—including all processes where acid-forming oxides of nitrogen are evolved.
(e) Works in which mineral phosphates are treated with acid (nearly all these are fertilizer works).
(f) Gas Liquor Works. Tar Distilleries.
(g) Chlorine Works in which chlorine is made or used.
(h) Muriatic Acid Works including all processes in which hydrochloric acid gas is evolved.
(i) Sulphide Works including all works in which sulphuretted hydrogen is evolved.
(j) Refineries in which benzole, shale oil or crude petroleum are refined or in which further refining of the product may cause evolution of gaseous sulphur compounds.
(k) Works in which oxides of sulphur are evolved in any chemical process.

VOL.
1
958/9

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VOL
1
1958

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Reports on Meetings

Air pollution and the iron and steel industry

Report of a conference held in London during September 1957
by the Engineers' Group of the Iron and Steel Institute

(*Received* 20 *December* 1957)

DISTRICTS where the principal manufacturing industries are the processing of iron and steel are traditionally notorious for their highly polluted atmospheres. A smoking stack has, in the past, been considered indicative of a prosperous period in the industry. The high degree of pollution is partly due to domestic sources, since steel towns are frequently situated near a coal field and have adequate supplies of cheap coal for domestic consumption as well as for the industrial processes and their ancillary services.

The 2 day conference held by the Engineers' Group of the Iron and Steel Institute discussed in detail the various methods that can be used to reduce substantially the pollution arising from the different sources within the works. In modern plants the serious sources of black smoke have been largely eliminated. Raw blast-furnace gas is no longer vented to the atmosphere, but is carefully cleaned prior to heating other parts of the plant; reheating furnaces are usually oil- or gas-fired; smoke is no longer considered necessary to provide the reducing atmospheres in heat-treatment furnaces and the older steam cranes and locomotives on the works site are being replaced by diesel or electric equipment.

However, in recent years the introduction of steel-making processes using oxygen enrichment have created new problems. The particles of the orange-brown fume produced are extremely fine and vary in size range, depending on the process employed during their formation (Fig. 1).

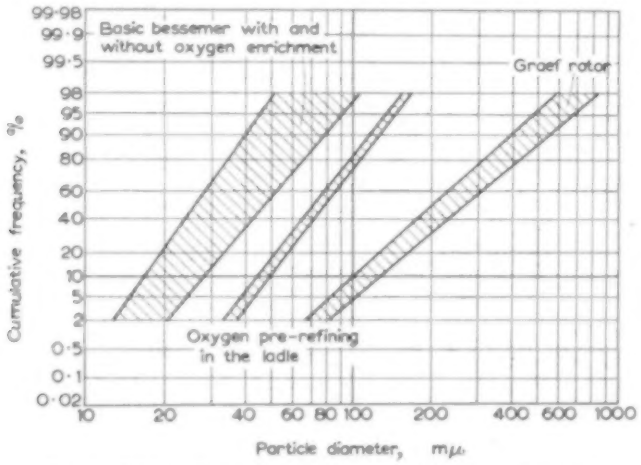

FIG. 1. Distribution of sizes of fume particles from the various oxygen steel processes.

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Highly efficient collection plants, which in some cases have to operate at high temperatures and in corrosive atmospheres, are required. The most difficult combination of these is encountered in the

oxygen steel-making process developed at the Vereinigte Österreichisch Stahlwerke A.G., Linz and at the Österreichisch Alpine Montan Gesellschaft, Hütte Donawitz, which is known as the Linz–Donawitz process.

The process entails blowing a mixture of about 80 per cent oxygen-enriched air through a tuyere on to the surface of the melt in a refractory-lined convertor with a capacity of about 30 to 40 tons. Outgoing gases, which consist mainly of carbon monoxide, continue to burn with the excess air and temperatures of the order of 2000°C are not uncommon. Commercial gas-cleaning plants, however, usually operate in the range to 200°C. The gas volumes to be treated are about 100,000 ft³/min. Although some excess air is unavoidable, it has been possible to reduce the volume to be treated to about one quarter of this, and the dust loading is then about 8 to 13 g/ft³. By using a high-pressure waste-heat boiler and electrostatic precipitators the engineers at Donawitz have not only reduced the outgoing fume concentration to less than 0·044 g/ft³ but have made the heat and fume recovery an economic success.

Fifteen papers were presented at the conference, the majority dealing with the application of standard methods of dust and fume removal to the wide-variety plant encountered in the various phases of iron and steel manufacture. The titles of the papers, the authors, and a brief survey of the scope of each, are given here.

External dust deposition and sulphur emission: H. G. JONES and J. T. DAVIES (Steel Company of Wales Ltd.).

Dust deposition, measured with modified deposit gauges, and sulphur concentrations, measured with DSIR lead peroxide candles, have been surveyed in and around Margam works. It has been shown that serious pollution (deposition in excess of the relative rate of 50 tons/mile² per month; SO_3 in excess of 1 mg/day per 100 cm² lead peroxide) occurs almost exclusively within the works area.

External pollution from an iron and steel works and measures towards its reduction: S. H. BROOKS and W. J. CALVERT (Appleby-Frodingham Steel Co., Ltd.).

Measures have been taken at Appleby–Frodingham, an integrated steel works, to reduce the emission of coarse dusts and fumes. Van Tongeren cyclones have been installed on the ore drying plant, and multicyclones have been built on the sinter plant. The shunting locomotives have all been fitted with a smoke consuming device, which is fully described. The possible methods of combating pollution from other sources, in particular the open-hearth furnaces, are discussed, but after considering the damage from these sources it may be found difficult to justify the expense of reducing pollution much below the present level.

Mitigation of air pollution in sinter plants: A. H. MEADLEY, J. G. COLVIN and H. J. CAMBLE (Stewarts and Lloyds Ltd.).

At the Corby works of Stewarts and Lloyds investigations have been carried out over the past 8 years to find the degree of dust dispersal from the various points in a sinter plant. The most suitable equipment to deal with the relatively coarse dust (only 36 per cent is less than 76 μ) has been found to be the " centicell " type multicyclone. This has also appreciably increased the life of the exhaust fans and ducts.

A pilot plant for the removal of iron oxide dust from the fumes arising in the pre-refining of iron with oxygen: L. G. SEPTIER (Steelworks Department of the Institut de Recherches de la Sidérurgie).

The injection of oxygen into liquid pig-iron in the ladle with a water-cooled lance leads to the emission of copious red-brown fumes, which are principally fine particles of iron oxide (Fig. 1). A pilot plant for fume recovery was installed by I.R.S.I.D. at the Mondeville plant for the Société Metallurgique de Normandie in 1953. It consisted of a dry multicyclone followed by a wet venturi scrubber. The unit proved to be more than 99 per cent efficient under industrial conditions. Sampling at the plant was by means of a specially devised collection train, using a filter thimble as primary collector. It is not stated whether a full-scale plant is in operation.

Gas cleaning in relation to oxygen pre-refining and the rotor process at Oberhausen: A. BERENDT (Hüttenwerk Oberhausen A.G.).

Oxygen pre-refining in the ladle and the Graef rotor process (which was developed at Oberhausen) both give rise to the characteristic brown fume, which is about 90 per cent Fe_2O_3, and varies slightly

as regards particle size range, depending on the process (Fig. 1). The fume abatement characteristics of a number of pilot plants were studied. A disintegrator scrubber and an irrigated turbo-collector both failed due to erosion, although the life of the latter unit was extended by installing a cyclone in series as a primary collector for coarse particles. Prior to their failure, these units did not give a satisfactory degree of cleaning. A venturi scrubber also was inadequate. An electrostatic precipitator cleaned the gas, but failed after a short time due to corrosion. A bag-filter pilot plant, using glass fibre supported on Orlon cloth, proved very successful. A full-scale plant using Diolene (a polyester fibre), the life of which has exceeded fourteen months, was subsequently constructed.

Operation of electrostatic precipitators on open-hearth furnaces at the Fairless works: E. B. SPEER (United States Steel Corporation, Fairless Works, Pennsylvania).

To reduce the air pollution at the Fairless works, which is in open country, the 330 ton open-hearth furnaces have been fitted with plate-type electrostatic precipitators. The plates are 18 ft wide, 17½ ft high and ¼ in. thick, and are spaced at 10 in. intervals, with eighteen plates across the precipitator chamber, forming seventeen lanes through which the gas must pass. The precipitated dust on these plates is removed periodically by an air-vibrator rapping system. The discharge electrodes are $\frac{3}{16}$ in.^{2} steel wires, 19 ft long, suspended at the centres of the gas lanes formed by the collecting electrodes and are negatively charged to 65 kV. There are 10 wires per lane per field, a total of 170 wires per field; and a total of 1020 wires in the chambers comprising one precipitator.

The chambers were designed to handle 75,000 ft^3/min at 300°C and a normal dust loading of 0·8 g/ft^3 with a 98 per cent efficiency. The higher dust loading of 2·5 g/ft^3 during oxygen-lancing is reduced to 0·05 g/ft^3 by the precipitators, while the outlet gas when blowing the chequers contains only twice this concentration. Dust collection from the precipitator hoppers is by a suction-line system leading to a primary and a secondary cyclone followed by a venturi scrubber, all connected to a common hopper. The dust is thoroughly wetted here to simplify disposal. The most serious difficulties occur during the lime and ore boiling periods, when a faint brown plume still exists. Recent improvements have been automatic power regulation and controlled corona discharge electrodes, which double the efficiencies under high-loading conditions.

Those attending the Conference were much impressed by coloured photographs showing the complete removal of the brown fume when the precipitators were switched on.

VOL. 1 58/9

Waste-gas cleaning systems at oxygen steel plants: A. VACEK and A. SCHERTLER (Österreichisch Alpine Montan Gesellschaft, Donawitz).

Some of the tremendous problems associated with cleaning the gases from the Linz–Donawitz process are presented in the introduction to this review. At Donawitz the effectiveness of various scrubbers (a disintegrator, a venturi, and an impaction scrubber) and of dry filters (slag wool, coke, electromagnetic and electrostatic) were tested, but only the Waagner Biro eddy type filter and the Lurgi electrostatic precipitators were found to give satisfactory performances. The method chosen here is the electrostatic precipitator, as the wet washer requires a ready supply of water on the site. Other general considerations are the space available for the plant, the method of dust utilization and the statutory limits imposed on the waste gases. It has been found that the installation costs of a dry electrostatic precipitator and a wet system with water recovery are about the same, but the operating costs are about two to one in favour of the electrostatic precipitator. If a 10 year amortization period is allowed for the cleaning system and the waste heat boiler, the saving in heat recovery is greater than the operating costs and amortization, and so overall production costs are lowered.

Cleaning of fume from arc furnaces: A. S. HIPKIN (Visco Engineering Co., Ltd.).

Suggestions, based on the author's experience, are made for the installation of dust collection plant on arc furnaces.

Dynamic dust and fume precipitators: F. WRIGHT (Air Control Installations Ltd.).

The "Rotoclone" type turbo-collector and hydrodynamic gas-washer are described. The latter unit has been installed as a dust-collection system on a close-hooded electric arc furnace, but it is doubtful, considering the efficiencies given for this type of scrubber, whether it will be highly effective in dealing with the fumes during oxygen lancing.

Mitigation of smoke, dust, and grit at coke-oven plants: G. W. LEE and J. P. GRAHAM (British Coke Research Association).

Sources of pollution in coke-oven plants are the charging and discharging of the ovens, leaks from the ovens during carbonization and during the quenching of the coke. Careful design of the oven doors and charging machines and dry quenching of the coke alleviate the pollution.

The extraction of sulphur from coke-oven gas and the manufacture of sulphuric acid: P. H. PURCELL and T. H. WILLIAMS (Stewarts and Lloyds Ltd.).

At the Corby coke-ovens the coke-oven gas is desulphurized by the Collins ammonia process, and sulphuric acid is produced by the Chemiebau wet-contact process. The plant was designed to handle 35,000,000 ft^3/day, but at present washes only $2{\cdot}95 \times 10^7$ ft^3/day, the output of the coke oven plant. The liquor-flow rates and concentrations, and other design data are given, as well as improvements which have been incorporated on other plants as a result of the experience with this one. These include a simplified liquor-recirculation system, the use of pure aluminium in the construction of the deacidifier, and Raschig rings instead of bubble trays and caps. The sulphuric acid from this plant can be produced at a price which compares favourably with that by other methods.

The Fulham–Simon–Carves process for the recovery of sulphur from flue gases: T. KENNAWAY (Simon–Carves Ltd.).

In this process the waste gases containing the oxides of sulphur are scrubbed with ammonia liquor from gas works or coke-oven plants. The solution of ammonium sulphate, sulphite, bisulphite, and thiosulphate is converted to ammonium sulphate and sulphur by autoclaving. An account is given of development from pilot plant to the full-scale process. This process, as distinct from ordinary flue-gas washing, produces ammonium sulphate and elemental sulphur, which offset the operating cost of the plant. However the capital cost of the plant is rather high.

The complete elimination of dust from gases at 300–400° C: H. L. RILEY (United Coke and Chemicals Co., Ltd.).

The construction of a multilayer glass-fibre filter for high-temperature filtration is discussed. This has been successfully employed for removing dust from the naphthalene oxidizers in the phthalic anhydride process.

Measurement of dust in flue gases: R. JACKSON and R. A. GRANVILLE (British Coal Utilisation Research Association and the British Iron and Steel Research Association).

A detailed description of the B.C.U.R.A./B.I.S.R.A. flue-gas sampling equipment, which can be used at high temperatures, is given. This has been used to measure the dust concentrations in a sinter plant, a producer-gas main, and an open-hearth furnace.

The capital costs of some waste-gas cleaning plants for use in iron and steel works: R. A. GRANVILLE (British Iron and Steel Research Association).

The capital costs of some commercial gas-cleaning plants are presented in graphical and tabular form. The data, which were obtained by direct enquiry to the manufacturers of the several types of plant, relate mostly to electrostatic precipitators.

The discussion of the papers emphasized the enormous expenditure by the industry in attempting to solve its air-pollution problems. The conference showed that these problems could be tackled efficiently and that in some cases an economic solution could be found. There are many technical difficulties which remain to be overcome, but ultimately the iron and steel towns in the future will no longer merit their traditional reputation.

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VOL
1
1958/

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Air pollution symposium at Cincinnati

Report of a symposium held at Cincinnati from 4 to 6 November 1957
at the Robert A. Taft Sanitary Engineering Center
(*Received February* 1958)

THE Robert A. Taft Sanitary Engineering Center is in a fine new building over-looking the Ohio River outside Cincinnati. In consequence of the U.S. Air Pollution Act of 1955, the Center has extra responsibilities in air sanitation on behalf of the U.S. Public Health Service. Acting as co-sponsor with the American Geophysical Union, the Center has recently performed an international service in bringing together some of the widely scattered groups who have knowledge of particular sections of the problem of atmospheric pollution. Dr. J. P. LODGE, Chief of Chemical Research at the Center, as well as Committee Chairman of the American Geophysical Union, organized the meeting and acted as Chairman. Many States of the U.S. were represented, as well as Canada, Mexico, Australia, Britain and Sweden. This Symposium on Atmospheric Chemistry of Chlorine and Sulfur Compounds from 4 to 6 November 1957, contained " something old, something new . . . " and produced some useful and well-integrated contributions on a specialized but growing subject. An account of the discussions and original papers read will be the responsibility of the Center and the authors concerned, but a brief survey of the problems they revealed can be given here.

Sulphur and chlorine compounds in the atmosphere are studied because even in small amounts they may provide nuclei for the formation of cloud and fog, and because in greater concentrations they may do damage. They exist in three phases as solids, solutions, and gases; and at least three chemical changes (a decrease in Na : K ratio, the oxidation of sulphur compounds to SO_2, and the combination of sulphur compounds with ammonia) are important.

Sampling and measurement may be by crude or refined techniques according to requirement. (1) For particles or droplets containing dissolved chemicals the gelatin reagent film is valuable because the area of the discoloured circle seen under the microscope is proportional to the mass of chemical in each particle. The reagent dyestuff in the film can be chosen to respond to one particular ion such as Cl^- or SO_3^{2-} in the particle. (2) A means of applying text-book analytical methods to individual particles is the use of micrurgy, involving micromanipulators and microtools viewed under the microscope. The particle, on the undersurface of a slide, is covered with a drop of oil, and micropipettes, etc. are introduced through the oil. (3) A physical way of identifying hygroscopic particles is available, if they are fairly pure chemicals, by observing the relative humidity at which they go into solution. The particles are captured on spider webs and held in a microscope field in an air stream of variable temperature and relative humidity. The change from crystal to droplet is quite sharp and striking. (4) Several spectrophotometric methods are applicable to samples of solid or dissolved material extracted from the air. (5) Systematic diaries of bronchitis patients are now giving useful information about the incidence of troublesome amounts of atmospheric pollution.

The distribution of chloride salts over the North American continent and Australia has been studied with aircraft and various sampling and measuring devices. Chlorides are found in similar amounts at all altitudes and depend ultimately on the occurrence of gales at sea (in Britain there are also appreciable quantities of chlorides from the combustion of coal). The surprising result seems to be emerging that, once they are well up into the atmosphere, chloride particles persist for many days. Variations of chloride concentrations beneath clouds have been observed. Solid matter from the atmosphere found in solution in deposit gauges continues to be studied.

The only compound in the gaseous phase that was considered was SO_2. It can be separated from other sulphur compounds by one of several physical or chemical processes at the time of sampling. The analytical methods involving titration or ionic conductivity can be made automatic. Little work has been done on the study of SO_2 at heights in the atmosphere. Perhaps this is unattractive because the amount of SO_2 is likely to be affected by so many factors: wind trajectories, turbulence, and variations of source, coupled with its relatively short half-life.

The transport of SO_2 downwind from the high smoke stacks of giant power stations is being studied

VOL.
1
58/9

and compared with formulae based on density and velocity of stack gases, and eddy diffusivity. The symposium received calculations and speculations about the life history of atmospheric pollution (1) in a downwind from a large town, (2) in a region of water fog, (3) over Britain as a whole, and (4) in the earth's atmosphere as a whole.

Some of the problems involved in the removal of SO_2 from flue gases were considered, especially the advantages and practicability of removing it by surface reaction with hot solids.

The following papers were read at the Symposium:

Hygroscopic particles in the atmosphere and their identification by a phase-transition method: S. TWOMEY (Commonwealth Scientific and Industrial Research Organ. Sydney, N.S.W.).

Techniques for the determination of halides: N. H. FARLOW (Naval Radiological Defense Lab. California).

Micrurgic identification of chloride and sulfate; Kinetics of the reaction between ammonia and sulfuric acid aerosols: RICHARD D. CADLE (Stanford Research Institute, California).

Techniques of precipitation analysis; The atmospheric budget of chlorine and sulfur: ERIK ERIKSSON (University of Chicago, Illinois).

Spectrophotometric determination of chloride in air: PHILIP W. WEST and HANS COLL (Louisiana State University).

Techniques for measurement of hydrogen sulfide and sulfur oxides; Concentrations of sulfur-containing pollutants found in a major urban area: MORRIS B. JACOBS (Dept. of Air Pollution Control, New York).

Determination of sulfur dioxide in the atmosphere: G. C. GAEKE, JR. (Kem-Tech Laboratories, Louisiana) and P. W. WEST (Louisiana State University).

Improved titrilog sensitivity: J. S. NADER and J. L. DOLPHIN (Taft Engineering Center, Cincinnati).

Improved titrilog sensitivity. Part II. Field performance and evaluation: HERBERT C. MCKEE and W. L. HOLLWITZ (Southwest Research Institute, Texas).

Sulfur dioxide removal and control: DANIEL BIENSTOCK and HOMER E. BENSON (Bureau of Mines, Pittsburgh, Pa.).

Transport of sulfur dioxide from point sources: F. E. GARTRELL (Tennessee Valley Authority).

Calcium-sulfate relationships in atmospheric particulate matter: J. L. MONKMAN (Dept. of National Health and Welfare, Ottawa, Canada).

The status of air pollution measurement in Great Britain: P. J. LAWTHER (Medical Research Council, London).

Chloride particle measurement in the south-western United States: W. D. CROZIER (New Mexico Institute of Mining and Technology).

Chloride and sulfate particles in the atmosphere: HORACE R. BYERS (University of Chicago, Illinois).

Artificial cloud nucleation with sodium chloride: E. M. FOURNIER D'ALBE (UNESCO Mission, Mexico).

Kinetics of the oxidation of sulfur dioxide on particulate matter; Some inferences from the analysis of precipitation water: CHRISTIAN E. JUNGE (Air Force Cambridge Research Ctr., Massachusetts).

The half-lives of some of the atmospheric species: A. R. MEETHAM (National Physical Laboratory, Teddington, England).

Some inferences concerning the total atmospheric budget of marine aerosols: A. H. WOODCOCK (Woods Hole Oceanographic Inst., Massachusetts).

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VO
1
1958

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Atmospheric diffusion and air pollution

Report of a conference held at Oxford in August 1958

AN international symposium on atmospheric diffusion and air pollution took place in the Clarendon Laboratory, Oxford, from 24 to 29 August 1958. It was sponsored jointly by the International Union of Theoretical and Applied Mechanics and the International Union of Geodesy and Geophysics. The Chairman was Sir GEOFFREY TAYLOR and the Secretaries were Dr F. N. FRENKIEL and Professor P. A. SHEPPARD. Hospitality was extended to the conference by Queen's College, Oxford. The congress was attended by about 150 delegates from 20 countries, and over 30 papers were presented. In this review the subject will first be surveyed and then we shall discuss how far answers to the problems reviewed will be found in the proceedings of the conference when they are published and made generally available. A detailed discussion of individual papers will not be attempted because this will be more profitable when they are available in print, as it is hoped they will be in a few months, together with a report of the discussions which took place.

The motion of the atmosphere may *transport* a great variety of things and in a variety of ways. *Momentum* may be carried from one layer to another by the eddying motion in a way which is not fully understood because pressure forces can act on parcels of air without any exchange of substance. *Heat* may likewise be transported but except for radiation and molecular processes it is only injected into a portion of air by an admixture of warmer air. However there are buoyancy forces acting upon the warmer air which may, and often do, influence the motion effecting the transport of heat. This is not the case with pollution such as tiny smoke and dust particles, and pollutant gases in small concentrations such as SO_2, for these are effectively *passive pollution*, and a knowledge of the air motion would enable one to predict their spread. *Falling particles* come in two main categories, those which are so *dispersed* that their fall can be approximately superimposed upon the air motion in order to determine their dispersion, and those, such as rain and snow, which are often concentrated into *showers* in which the added weight of the particles produces a bodily movement of the air by the overlapping of the wakes of the individual particles. Finally there are *particles which undergo a change while they are airborne*. They may be affected by sunlight, as is nitric oxide from which ozone is produced; ozone is not emitted as such but is a major noxious component of Los Angeles smog. They may undergo changes in the presence of water vapour by forming droplets in which chemical reactions occur, or they may react on the surface of airborne solids. Particles may coagulate and become falling ones. Radioactive particles may decay while they are airborne.

Some airborne pollution may be released only under special circumstances. Ragweed pollen is blown from the plants at certain times of year and mainly in certain types of weather which have their own special diffusion properties. Industrial and domestic pollution has a great diurnal and seasonal variation in output. Finally particles may be deposited in a variety of ways. They may be deposited on vegetation, possibly in a manner dependent upon the weather. They may be washed out by rain either by acting as condensation nuclei for the embryonic rain drops or for the other droplets which are swept out of the air by rain. They may be deposited upon solids which are washed out, or carried with the water vapour by Brownian movements on to growing droplets. They may be removed by chemical reactions on suitable surfaces, deposited by thermal precipitation, filtered out in noses, or condensed on to cool solids or liquid surfaces.

All forms of pollution are subject to the air motion, and this must therefore be the first and main object of study. We should start with passive pollution, and this means having some idea of the track of a particle of air. Clearly this must be a statistical result because tracks vary greatly with place and time in such a way as to produce what we call diffusion. But the first problem is that we cannot normally measure such tracks except with the greatest difficulty. The measurement of the beginning and end point of tracks is not enough foundation for a theory of the tracks themselves, so that some measurement of the wind fluctuations is required. But this can only be done at fixed places and not by following particles, and the derivation of tracks from measurements of fluctuations at fixed points is a problem of major importance and difficulty.

VOL.
1
958/9

It is of course particularly difficult to measure the motion at more than 100 metres or so from the ground, and most measurements have to be made at altitudes lower than about 10 metres. At the surface there is an exchange of momentum and pollution between the ground and its covering and the air above. Ultimately this must be *effected* by molecular processes and it is important to know how far the total exchange between the ground and the air is *governed* by the magnitude of the molecular processes. Are they always adequate to the occasion, or do they exert a major control over what takes place above?

In the lowest few metres the motion is primarily affected by the buoyancy produced over hot ground or the stability produced over a cold surface, the wind speed, and the roughness of the surface. The simplest number which relates these factors is the Richardson number, which is a ratio between the inertia forces arising from the shearing flow and the buoyancy or stability forces. But is this the only number which it is necessary to specify in order to determine what kind of flow—smooth or convective—will occur, even assuming that the Reynolds number (governed by the molecularly produced stresses *at* the surface) is unimportant? For as we ascend from the ground we quickly find that the controlling factors become the earth's rotation and the pressure gradient as expressed in isobar maps. The relevant non-dimensional number is then a new kind of Richardson number which turns out to be related, through the earth's rotation and gravity, to the relative magnitudes of the horizontal and vertical temperature gradients.

As we rise still higher we become conscious of weather systems whose size and manner of fluctuation is governed by a variety of new factors which include the height of the tropopause, the amount of cloud and the latent heat of water, the size of the earth, the distribution of land, sea, and mountains and the length of the day coupled with the strength of sunshine and the radiative properties of air which ultimately remove into space the heat fed into the atmosphere by the motion upwards from the ground and sea.

It is clear, therefore that there are many types of motion in the atmosphere: in the study of how many are we making evident progress?

All these problems are of great complexity and require considerable mathematical skill for their solution even in their simplest form. Some are quite intractable and we have to be content with the mathematical solution of a problem which is slightly different. At this point there are two temptations, the first is to apply the results obtained far beyond the field in which it is valid, and the second is to ignore those instances for which we have no solution. The solved problems may be the most important and interesting to those working in the field, but nature will not wait until phenomena are understood before they happen, nor can the community avoid them.

There are two types of equation that are particularly tempting to the theoretician: those which describe diffusion as if it were some form of conduction (such as heat in solids), and those which liken it to some sort of transmission such as sound waves in air. These two have one distinct difference in that sound waves have a distinct boundary beyond which they are not detectable until a definite lapse of time since emission from the source, whereas heat conducted through a body arrives—at least according to the equations—immediately with imperceptible magnitude and increases gradually.

The technique devised by Reynolds for describing turbulent motions in terms of a mean, steady flow, and fluctuations around the mean superimposed upon it, is very satisfactory in wind tunnels and the like where the maximum duration and extent of a fluctuation is small. The mean value can then be defined and can be regarded as (or made) steady. But in the atmosphere the motion is not steady on any time scale so that Reynolds' method fails in many cases. Have we any more powerful method?

Most of the experimental techniques for measuring fluctuations in the laboratory have been tried out of doors with varying degrees of success, but have we any new methods of following and determining the motion?

If we are only just becoming properly conscious of the formidable task before us we must be forgiven if many of these questions have merely been thrown around at a conference such as this. The contributors came chiefly with old techniques and ideas but certainly departed with a new humility and awareness of their limitations, and it is hoped that in the pages of this journal the fruits of this awareness will blossom.

No new work on the behaviour of pollutants was reported. The title of the symposium should be taken to mean that atmospheric diffusion and its applications to pollution were the subject, not the properties of pollution. A few papers discussed the dispersion of falling particles but none the case

VOL 1 1958

in which the motion was affected by them. The problem of deposition was scarcely touched upon.

By far the majority of the papers were on techniques of studying turbulence and theoretical ideas connected therewith. The optimism, often shown, that the theories of homogeneous turbulence will yield useful results does not seem justified; and in view of the complicated nature of the problem the most profitable line seems likely to be one of empiricism enlightened by the theoretical ideas rather than a formal use of the theories which are often grossly naive.

The atmosphere has now been explored very extensively in the lowest few metres and no startling new progress seems likely for a long time. But on a large scale our ignorance of the facts of the motion necessary for a theoretical advance is so great that new techniques of observation are almost bound to lead to considerable steps forward. The most outstanding example of this is the use of radioactive isotopes of elements of comparative rarity in the atmosphere which are produced naturally by cosmic rays, chiefly in the stratosphere. For instance beryllium 7 and phosphorus 32 are both created in this way at a rate known from the distribution of cosmic ray intensity throughout the atmosphere. Their decay rates are different and are accurately known. Consequently, because air remains in the stratosphere often for years without any excursion into the troposphere the relative densities of the two isotopes can be computed for the stratosphere. In the troposphere, which is well stirred and in receipt of less cosmic radiation and also subject to loss by removal by rain, limits which are very different from the stratospheric value can be set. In this way stratospheric air which has recently entered the troposphere can be recognized and the rate of removal of radioactive substances from the troposphere by rain calculated.

This is a substantial step forward in the solution of the problem of how quickly the store of strontium 90 in the stratosphere, put there by H-bombs, will be deposited on the ground. It will also give us new knowledge about the rate at which the air in the stratosphere is exchanged between the equatorial and polar regions. Previously such substances as ozone and water vapour, which carry much less information about their history with them than decaying isotopes, had to be used. Already some dearly held views about the stratospheric circulation look like having to be abandoned.

At scales in between those of diffusion in the lowest few metres and the circulation of the whole atmosphere there was a depressing lack of substantial progress to report. There seemed to be a widespread unawareness of the problems of pollution on the large urban and provincial scale. An unexpected suggestion came from Mexico City, which promises to smother itself in a Los Angeles type of smog unless something is done, namely that carbon dioxide might be the best tracer to use in studying the urban pollution there because for various reasons other pollutants are unsuitable. But the otherwise barrenness of the conference in this respect is due to a silent recognition that this is a more complicated problem than the larger and smaller one, and also to a consciousness that its solution is probably a social rather than scientific one, for no theory can reduce the abominable output of many of our cities—that is a matter of the will of the community.

In conclusion therefore, the published proceedings are likely to appeal most to the student of turbulence theory and the experimental physicist and one is led to wonder whether a conference on air pollution and atmospheric diffusion might not be profitable in a year or two's time, at which emphasis can be laid on those problems of which we have only been reminded.

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VOL.
1
58/9

Int J. Air Poll. Pergamon Press 1958. Vol. 1, pp. 139–142

Book Reviews

H. L. GREEN and W. R. LANE: **Particulate Clouds.** Spon, London, 1957. 424 pp., 70s.

THE sub-title is " Dusts, Smokes and Mists—their physics and physical chemistry and industrial and environmental aspects ". The first part, consisting of eight chapters, deals with the physics and physical chemistry. After an introduction, the second chapter discusses the production of particulate clouds and how the particle size is determined in each method. The third discusses a variety of physical characteristics, the most important of which are rate of fall of the particles, Brownian movements, electrification, and evaporation. Next is a chapter rather on its own dealing with optical properties, and the fifth discusses the important problem of coagulation. " Deposition and filtration " and " sampling and estimation " are the topics of two less fundamental chapters dealing with various practical methods of studying particulate clouds rather than with the clouds themselves. The eighth chapter, on diffusion in the atmosphere, discusses diffusion of clouds in a theoretical atmosphere rather than the complexities of the actual one.

The second part on industrial and environmental aspects begins with a chapter on collection and precipitation. We then move into a rather different field—health hazards, followed by a chapter on atmospheric pollution where again we learn more about the measurement and effects of airborne pollution than about the processes of transport by the atmosphere. In chapter 12, on aerosols in nature, there is a discussion of natural water clouds with the emphasis again on the clouds rather than on how the atmosphere produces them. The final chapter is a summary of various uses of particulate clouds.

It will at least be clear by now that this is a very considerable and important book. It will undoubtedly be a very valuable work of reference for some time and the authors are to be commended most highly on their achievement. The range of topics covered is so wide that, in performing their service of gathering the material into one book, a vast literature has been covered. In an outspoken preface, the authors criticize strongly the writing up of the same material in several different places and the publication of " massive volumes of symposia containing the same contributions in slightly different form plus verbatim reports of discussions " because of the well-nigh intolerable burden imposed upon the searcher for information. The search now having been made, the reader of this book is given a flying start because the references are copiously set out at the end of each chapter.

However, the magnitude of the task of searching makes it very difficult for the authors to remain critical, to extract those parts of a paper which will form a basic element in future thinking and to ignore ruthlessly the less important. They tend to chronicle rather than teach. This reviewer is far from competent to criticize the treatment in every chapter. He finds the greater part of the book most valuable and well-written but, on those topics with which he is most familiar he does, in the present instance, find the authors disappointingly uncritical. It is suspected that this is because these are the fields in which the authors are least qualified to write. Their work is not made any easier for having to go to review papers and it may well be that, when that happens, it is a signal for the authors to abandon the chase—after all, atmospheric diffusion is an enormous topic on its own in the absence of particulate clouds and natural clouds of water and ice have a behaviour peculiar to them which results from the large latent heat and the great variations of pressure and temperature to which air is naturally subjected. It cannot be argued that these topics are included for completeness' sake: the book is not complete anyway. For instance, pulverized fuel is not discussed, nor the problem of spraying locust swarms, nor fluidized beds of particles, nor catalysts. The choice must obviously be the authors' own: but it is often more profitable to write at greater length on subjects in which they have authority rather than give the effort to mugging up borderline subjects and including them in order to give a " more balanced treatment ". Without working in a field for years, one cannot easily see which way the subject is turning so that the balance of today may quickly be upset by developments which the authors were unable to perceive or anticipate. In any case, would one go to a book of this nature for information on rain-making?

These remarks should be interpreted to mean that the achievement is so impressive that, when the time comes for a second edition, it is hoped that the authors will spare themselves a little by leaving

VOL 1 1958/

out those topics which have grown beyond their reach and giving us more of their wisdom, which they alone can give, in their own special fields. Both they and their readers could have more fun this way too!

R. S. SCORER

The Air Pollution Handbook. Edited by P. L. MACGILL, F. R. HOLDER and C. ACKLEY. McGraw-Hill, New York, 1956. 680 pp., $15.

IT is an ambitious enterprise to compile an encyclopaedic book on air pollution when the subject is so little advanced. Undoubtedly many branches of applied science have been directed at a fairly advanced level to problems of air pollution: but very little has been done in the way of routine surveys. The nature of the problem, therefore, is largely unknown to specialists working on certain aspects of it. A cursory glance at this handbook is enough to remind anyone how little he knows about air pollution as a whole, however expert he may be in the techniques, either theoretical or experimental, which he has chosen to apply to it.

We may sometimes feel that the problem is so urgent in certain areas and so negligible in others that surveys, either national or international, seem scarcely appropriate: for they will not help us to solve the immediate problems which are mainly economic and social. But this is short-sighted and the chief criticism of the *handbook* is that it shows no consciousness of the need for the establishment of at least daily widespread sampling of air pollution. Air pollution has been part of climate in all parts of the world for a long time, and its importance is increasing as the atmosphere is used to an ever greater extent as a depository for waste (or uncontrollable) materials. If widespread surveys are begun now, within two or three decades we shall have accumulated a store of information on which future planning and social surveys can be based. At present the sampling is generally so unrepresentative that a special survey, usually short-lived, has to be made when an enquiry demands one. There is, for instance, no standard exposure for pollution sampling instruments like there is for thermometers and rain-gauges.

VOL.
1
58/9

But if routine chemical analyses of rain-water, sampling of airborne particulates and such-like are carried out the world over, the present problems of acute local pollution will remain. Because the producer of pollution often experiences so little direct economic incentive to abate it, the situation has been allowed to arise in which the cost of abatement is very large. Understanding and knowledge of the problems are consequently of great economic value. Until the publication of this handbook, there existed no nucleus of information. One of the reasons for this is that the study of air pollution had not become an applied science in its own right, so that research was reported upon in journals scattered so widely that no-one became aware of more than a fraction of it. The main justification of this present new journal is that there was hitherto no orthodoxy and no common meeting point in air pollution research. The only journals which have been mainly interested in air pollution have been propagandist and, therefore, generally not ready to publish research: none has, therefore, accumulated a working body of knowledge. It is fortunate that the handbook has preceded our journal because it can serve as a source book for researchers as they become aware of the wide field.

The handbook is good on the industrial side because equipment generally becomes internationally known fairly quickly. It is poor on the medical problems because these have tended to be of local interest and, being an American book, it has not drawn noticeably upon British experience in this respect. Bronchitis, lung cancer and pneumoconiosis are not mentioned. Again, the treatment of legislative problems only mentions as an item of history the Alkali, etc. Works Act in Britain which " has been effective in controlling pollution by heavy industry ". It is not generally realized in America that British legislation is far in advance of and more effective than any other.

That British pollution is great and well-publicized is due respectively to the intense concentration of population and predominant use of coal, and the greater public consciousness and smaller licence granted to industrialists. The notable achievement of the city of Pittsburgh in cleaning their atmosphere so that it is now probably no worse than that of Sheffield is to be measured in terms of speed and scientific methods used rather than in the absolute cleanliness of the air.

However, the sudden appearance of intense pollution problems in a country characterized by the rapid development of natural resources stimulated studies of appropriate urgency: and the handbook contains an enormous amount of valuable knowledge gained in this way. For it is much easier to see how dense local pollution introduced into clean air behaves if there is no other comparable source

to interfere. Evidently these situations have taught the authors of the chapters on meteorology how a meteorologist should view the difficult problems which face him. Indeed, the chapter on the physics of the atmosphere can be recommended to any serious student of meteorology whether he is interested in air pollution or not. In this, and in that on weather effects, the subject is treated in a refreshing way, so unlike many tedious texts which seem more interested in charts and theoretical atmospheres than in what we can see out of doors. Some readers, who know little meteorology to begin with, may find them somewhat stiff mathematically but they can be assured that the subject matter is important and worth-while.

One particular idea in these chapters is both important and interesting—that of " meteorological control ". This can mean, for example, that costly methods of pollution abatement are only applied when the weather is such as to make the pollution damaging. At other times, such as when the wind is fresh, no special abatement is attempted. In an extreme case, it might be necessary to shut down a plant while adverse weather prevailed. There is an inclination among legislators to think only of laws which are always in force. With a greater knowledge of the weather and its effects, they might achieve spectacular results by meteorological control.

There are other chapters of a less fundamental nature, such as those dealing with farm animals, plants, and visibility. That on epidemiology is rather general and brief. The strongest chapters, apart from meteorology, are on the physical chemistry, engineering, and experimental aspects. There is inevitably some repetition but this is often valuable when it is about something fundamental (but when will authors learn to ignore Donora, Meuse and London 1952?—spectacular disasters indeed, but mere incidents in the total problem!).

Many books are expensive nowadays. The Air Pollution Handbook is a bargain in comparison with books of a similar price by one or two authors or with those awful tomes containing the tedious proceedings of conferences with their often trifling discussions. Here there are fourteen substantial chapters, mostly carefully written, by a total of 31 authors, contained in about 680 pages of smallish type.

R. S. SCORER

C. N. DAVIES: **Dust is Dangerous**. Faber & Faber, London, 1954. xvii + 116 pp., illustrated, 21s.

VOL 1 1958

THE author states that his aim is to explain and classify the dangers of dust and to set out general principles for assessing and dealing with dust problems. In accomplishing this aim Dr. DAVIES has produced a volume which is a most useful introduction to industrial hygiene for the newcomer to the subject. Moreover the book will repay a reading by the practising hygienist inasmuch as here is a refreshing re-statement of the principles on which his science (or art?) is based. The bibliography of 169 references will guide the further reading of those whose interest has been aroused, and the comprehensive index will increase the value of the book to the reader who merely wishes to find a solution to a particular problem.

The outstanding section of the book is that which reviews the hazards to health which may arise when the industrial worker is exposed to dust and in particular when the dust is inhaled. The clarity with which particle size is discussed, in relation to the retention of dust in the lung and subsequent reaction, greatly facilitates the appreciation of the significance of the various methods of air sampling which are described.

Measures to prevent the inhalation of dangerous quantities of dust are discussed, and there are shorter chapters dealing with radioactive dusts, house and non-industrial dusts, and dust explosions.

The book is printed in clear type and well illustrated.

D. E. HICKISH

Kolloquium über meteorologische Probleme der radioaktiven Luftverseuchung (22–23 March 1957). Sonderdruck aus: **Beiträge zur Physik der Atmosphäre**. Akad. Verlagsgesellschaft MBH, Frankfurt A.M., 1958. 95 pp.

THE significance of this publication is not so much in the new information which it contains as in the fact that 34 West German meteorologists, nuclear engineers, and others assembled to show themselves

to be aware of the new pollution problem which faces society in the atomic age, and to equip themselves for dealing with it.

This publication contains thirteen papers, the first a general survey by Professor KOSCHMIEDER of the meteorological problems of radioactive pollution, the others dealing with methods of measurement of radioactive or other low-concentration constituents, diffusion processes in the atmosphere, the natural and artificial radioactivity of the atmosphere and their monitoring in a network of stations. They are mostly short surveys of existing knowledge on these subjects, with useful bibliographies where appropriate, but little of real originality is presented. The problems are mainly posed in conventional terms which few researchers will find exciting but for those primarily concerned with immediate, "engineering" aspects, the papers could be useful in providing within small compass a good view of modern methods and procedures.

Since the open literature on radioactive pollution is slender and dispersed it is well to have a booklet like the present in which such pollution is treated from different technical aspects. Much of the meteorology discussed is however not particularly directed to the behaviour of radioactive pollutants, which is fair enough. The most substantial paper presented, one by ROLL on "The exchange coefficient over the sea", is indeed quite far from obvious application to pollution problems, but the reviewer found it also the most stimulating. He would also particularly commend a portmanteau diagram by WIPPERMANN showing the atmospheric exchange coefficient as a function of spatial scale, time constant and characteristic velocity of the atmospheric disturbances responsible for mixing. It is a work of some imagination but admirably expresses the fact that turbulence is what we make it to be, and it should be particularly instructive to the physicist or engineer whose mind has been conditioned to the concept of a pre-ordained mean motion with the rest turbulence. It is timely because the radioactive pollution problem embraces air motions from the global scale downwards to the small eddies waving a plume from a factory chimney.

A useful enough volume then, but not exciting. To the halting reader of German, the diagrams in most papers tell more than half the story. But would that authors write summaries that truly summarize their work.

P. A. SHEPPARD

VOL.
1
58/9

R. S. SCORER: **Natural Aerodynamics**. Pergamon Press, London, 1958. vi + 312 pp., 22 plates, 60s.

BY profession Dr. SCORER is a mathematician but such a description is quite inadequate as a label for one who carries mathematics into so many fields. Apart from his high reputation among mathematicians, he is widely known among meteorologists, aviators, water engineers, physical geographers and among all those people of varied professions and interests who are concerned with problems of air pollution. Dr. SCORER makes mathematics live by seeking practical applications for it and he recognizes that people who do things, like wallowing in the atmosphere as the gliding fraternity do, can form sound opinions about such matters as the processes of energy transformation and thereby greatly assist in improving the mathematical formulation of difficult problems. He has also a happy gift of clear and expressive thought so that in his writings mathematics and physical reasoning are able to support each other without either appearing to obtrude at the other's expense.

In this new book Dr. SCORER develops the principles of fluid motion and takes his examples from the enormous variety of phenomena to be found in the atmosphere. The result is a book which can be recommended to meteorologists, to the student who wishes to acquire both a good introduction to aerodynamics and a lead to the many problems in which further progress is desirable, and to others whose work is dependent on, or perhaps at the mercy of, atmospheric conditions.

An introductory chapter on basic hydrodynamics, not however without its examples from nature, paves the way for a discussion in the second chapter of motion on a rotating earth, thermal winds, fronts and Sutcliffe's theory of development. This chapter is not altogether satisfactory because, attempting as it does to cover in a mere thirty pages a good proportion of what is known as dynamical meteorology, it clearly suffers from over-compression as well as from a few errors or inconsistencies in detail. There follow admirable chapters on Vorticity and Viscosity, each with its quota of arresting examples. In the succeeding chapters on Boundary layers, Wakes and Turbulence, Convection, Plumes and Jets, Waves, Clouds and Fall-out one would be hard pressed to think of any atmospheric phenomenon that is not illuminated by Dr. SCORER's treatment. He is indeed wealthy in comparisons

and allusions and provides much to satisfy all tastes, except perhaps that of the gourmet who may not like to read about his beloved spaghetti in a section describing the distortion of vortex tubes.

All these chapters, topic succeeding topic, are written in the stimulating and persuasive style for which the author is well known. Finally we come to a chapter on the Philosophy of Method in which he comments on the processes by which thoughts revolve in the mind of the mathematician, in that of the physicist and in that of the geographer. Here Dr. SCORER provides much food for thought and also many opening gambits for argument. This is certainly a most interesting chapter not least because Dr. SCORER has put so much of himself into it.

The interest and value of the text are greatly enhanced by the large number of diagrams and by 22 excellent plates many of which are the products of Dr. SCORER's skill and enthusiasm as a photographer. We offer a warm welcome to this book and wish it great success.

P. J. MEADE

P. AVY: **Les Aerosols**. Dunod, Paris, 1956. vii + 293 pp. (In French.)

THIS book represents a useful introduction to the study of aerosols. The emphasis throughout is mainly on general physical properties of aerosols, but attention is given to applications in industrial hygiene, meteorology, medicine and warfare. Other topics covered include explosion hazards, insecticidal aerosols and filtration of industrial smokes.

The author has concentrated mainly on the basic principles underlying our present knowledge on aerosols. (For example, there is a particularly clear discussion of the factors affecting velocity of sedimentation of particles in various size ranges.) However, despite the rather elementary approach, numerous references to the original literature are given and these should form a sound basis for a more detailed study of recent work in aerosol science.

G. A. H. ELTON

VO
1
1958

Air Pollution. Edited by Professor M. W. THRING, Professor of Fuel Technology and Chemical Engineering, University of Sheffield. Butterworths Scientific Publications Ltd., London, 1957. 248 pp., 42s.

ONE of the difficulties facing those who study air pollution is the number and diversity of the disciplines involved. The physicist, the chemist, several varieties of engineer, the climatologist, the botanist, the zoologist, the doctor, the public health official and the lawyer are among those whose expert knowledge is needed for the proper exploration of the subject. Many of them are represented in this volume; they had contributed lectures to a course on Air Pollution held at Sheffield University in 1956, under the aegis of Professor THRING, who has collected the material, after adaptation, to form a book.

The chief defect which results from the publication of lecture material of this kind is that repetition, while most useful in the spoken lecture series, is far from desirable in a book. When, as in this case, there is no index, the task of referring to a specific point is made troublesome. Another difficulty inherent in collecting a number of experts together is that the technical jargon of one may be quite incomprehensible to another and to the general reader. If the presentation is watered down to suit the general reader it loses its value to the man who needs the exact technical data; on the other hand a book in which so many points of view are represented must be directed to a fairly wide public, and it might logically be expected that the more esoteric details should be available in more specialized books or journals. This volume contains two such papers which were far above the reviewer, being largely mathematical, but which have been commended by those better qualified to judge.

The remaining chapters, while not of uniform standard, are of more general interest. The introductory chapter by G. NONHEBEL on the solid and gaseous constituents of air pollution is very good indeed. It is difficult to see how a more comprehensive and clearly defined account could have been given in such a short space. It seems a pity that Plate I and Plate IV were not printed in the same way (one is a negative and the other a positive form of the same type of picture) but this is a minor

point. E. T. WILKINS and W. F. B. SHAW, in the next two chapters, describe the instruments in general use for measuring pollution in the atmosphere, and smoke in chimneys, respectively. It would have been interesting to hear more about the latest additions to the range of instruments, even though they are not available for wide use at present, for the development of electronic devices is providing means for more detailed study.

J. PEMBERTON describes how air pollution can be detrimental to health, both in acute episodes such as the notorious " smogs " of recent years, and in long-term effects. Air pollution has also its effect on plant life, which is briefly summarized here. The publicity given recently to the plight of Oxford's buildings adds point to the next chapter, by R. J. SCHAFFER, on the effects it can have on stone and metals, and this is illustrated by photographs.

Having dealt with air pollution and its consequences, the book goes on to cover dispersion of the gases concerned. It is clear that what happens to the products of combustion must depend on climatic factors; these are themselves related to geographical and meteorological features. A. GARNETT, in a chapter which describes original research as well as much other information, deals convincingly with the complex interrelationships involved. She stresses the importance of the factor of local relief in the study of the regional effects of air pollution, quoting examples from the places in which smog disasters have occurred, and she recommends detailed studies to determine the probable effects before industrial development is carried out. The second of the chapters on dispersion is one already referred to as highly technical; in it C. H. BOSANQUET gives methods of calculating the flow of chimney gases and their concentration at ground level at various distances in different circumstances of wind velocity and buoyancy.

W. F. B. SHAW, in a chapter dealing with domestic heating, discusses the various fuels and methods of using them, but has little to offer the public-spirited citizen in the way of help in choosing appliances to reduce smoke, as he confines his descriptions to grates designed between 1816 and 1882 except for one large heating stove for the whole house. It is disappointing to be left with the impression that nothing has been achieved since then.

The next four chapters by A. FITTON on vehicle exhaust fumes, by J. W. BATEY on industrial boilers, by M. W. THRING on the iron and steel industry, and by J. WHITE on the manufacture of refractories, ceramics and cement, are largely descriptive of the various machines and processes and their part in producing pollution. Another technical chapter follows by C. HULSE on the choice of gas cleaning plant which deals in detail with all the different types of equipment, their advantages and disadvantages in performance. Finally A. MARSH and J. W. BATEY deal respectively with air pollution legislation prior to the Clean Air Act of 1956 and with the provisions of this Act itself.

This book includes so much that is relevant and of great interest and unobtainable in such compact form elsewhere that it deserves to be studied by all who have an interest in air pollution; its defects are largely those of the kind apparently indissoluble from multiple authorship and the transcription of lectures, and will not deter those who need the valuable information it contains.

MARJORIE CLIFTON

VOL.
1
958/9

PAPERS TO BE PUBLISHED IN FUTURE ISSUES

E. F. DARLEY, E. R. STEPHENS, J. T. MIDDLETON and P. L. HANST: Oxidant plant damage from ozone-olefin reactions.

FRANCIS T. FOX and LAWRENCE M. MARSHALL: Application of micro-diffusion of organic acids.

B. R. MORTON: The ascent of turbulent forced plumes in a calm atmosphere.

C. JEHANNO and C. LALLEMANT: Détermination de la pollution de l'air et de l'irradiation au sol, dues au " panache " d'un réacteur en marche normale.

R. S. SCORER: The behaviour of chimney plumes.

VOL
1
1958/

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OXIDANT PLANT DAMAGE FROM OZONE–OLEFIN REACTIONS*

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Abstract—The reaction of ozone with five-, six-, and seven-carbon olefins is quite rapid even in the gas phase at concentrations of a few p.p.m. These reaction mixtures produce a toxic material which causes damage symptoms on pinto bean plants which are indistinguishable from those attributed to oxidant-type air pollution. Ozonides, formed in small yield by this reaction, are stable materials which do not damage pinto beans in any way even at concentrations higher than those arising in ozone–olefin reaction mixtures or in outdoor air.

Evidence was obtained that the toxic material is unstable even at low concentrations in air. Its half-life appears to be no more than a few min. This result suggests that either a transitory ozone–olefin complex or an unstable zwitter ion formed by its decomposition is the actual toxic substance. Attempts to confirm this by adding excess aldehyde or sulfur dioxide to scavenge the toxicant were not successful.

INTRODUCTION

THE work of HAAGEN-SMIT *et al.* (1952) laid the basis for subsequent investigations on the rôle of ozone–olefin reaction products as important plant-damaging constituents of polluted atmospheres. These workers found that if any of a number of common plants were fumigated with the products of the reaction between ozone and a higher olefin, the plants would develop damage symptoms indistinguishable from those observed on the same plants exposed to the Los Angeles atmosphere during periods of heavy air pollution. Although some of these plants are susceptible to damage by other possible pollutants (e.g., fluorides, ozone, and sulfur dioxide), the symptoms produced by all other known plant toxicants are different from those produced by the ozone–olefin reaction products. This injury has since been designated as oxidant plant damage (MIDDLETON *et al.* 1957). The specific product or products responsible for it have not yet been identified. Because certain acid and aldehyde end products were not toxic in low concentrations, HAAGEN-SMIT and his co-workers concluded that an ozonide or related peroxide was the toxic factor. Thus it was stated: " The primary product, the ozonide, itself a peroxide, undergoes a series of changes leading to hydroxy and aldehyde peroxides and finally to aldehydes, ketones, and organic acids " (HAAGEN-SMIT *et al.* 1952). It was further postulated that structure of the olefin was an important determining factor in the formation of the phytotoxicant. To quote from this reference again: " For example, 1-*n*-pentene, which would furnish C_4 reaction products, is strongly active, whereas 2-*n*-pentene, yielding only C_2 and C_3 products, is inactive."

VOL.
1
58/9

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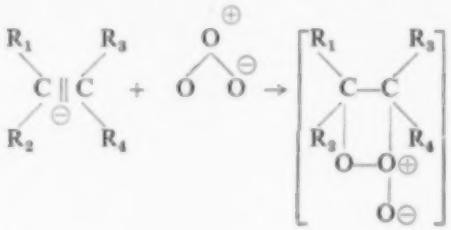
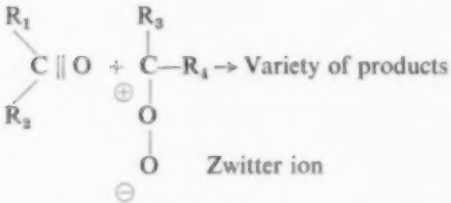
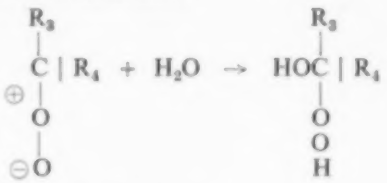
Recent studies of this reaction at low concentration, by use of the technique of long-path infrared absorption spectroscopy, (SCOTT *et al.* 1957) have shed new light on the mechanism and the products. This can be summarized by the CRIEGEE (1954, 1955) mechanism for this reaction:





where the R's can be alkyl radicals or hydrogen atoms. The addition complex (in brackets) decomposes to give an aldehyde or ketone and a zwitter ion which itself decomposes to give a variety of stable products. If R_3 is an alkyl radical and R_4 is a hydrogen atom then this zwitter ion is the same as the aldehyde peroxide mentioned by HAAGEN-SMIT while his hydroxy peroxide would be obtained (on paper at least) by addition of water to the zwitter ion:



The ozonides, which have the structure:

are formed in small yield only from the higher olefins, presumably either by rearrangement of the addition complex or by recombination of the two fragments into which it decomposes. Furthermore, the ozonides, except the very lowest members, are quite stable materials both in the liquid state and in the gas phase.

The program reported in this paper was undertaken to determine the structure of the phytotoxicant, its mode of formation, and its properties with the aid of long-path infrared spectroscopy.

VOL.
1
58/9

FIG. 1. View of interior of the Franklin Institute Mobile Air-Pollution Laboratory which shows infrared spectrometer and cell with plant exposure box mounted above the cell.

VOL
1
1958/

METHODS AND MATERIALS

The experiments were conducted in The Franklin Institute Mobile Air Pollution Laboratory located in South Pasadena. The laboratory houses a long-path infrared spectrometer used in the analysis of polluted atmospheres (SCOTT *et al.* 1957). A plant exposure box was incorporated into the air-flow system of the long-path cell, the air flow being modified to operate as a stirred flow reactor (Figs. 1 and 2).

The plant exposure box is essentially a glass tunnel 2 ft square and 4 ft long. The glass sides are held in a frame of polished channel aluminum. The ends of the box

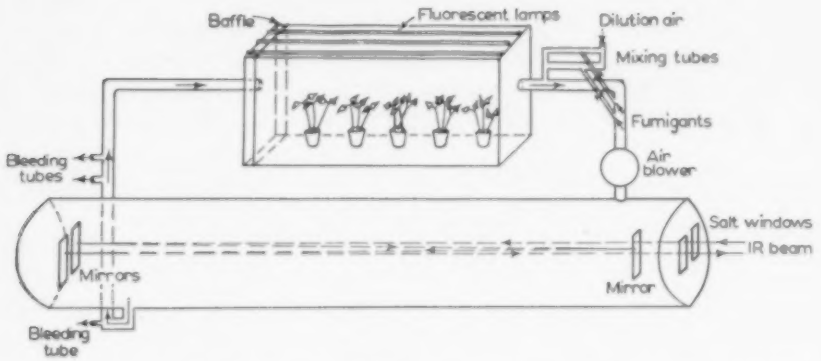


FIG. 2. Diagram of infrared spectrometer and plant exposure box which shows relative position and slurred flow reaction system.

VOL. 1 58/9

are closed with removable plywood covers; the inside of each cover is lined with aluminum foil in order to reduce the porous absorbing surface of the wood. Illumination of 1000 ft candles is provided for the plants during exposure by twelve 48 in. cool white fluorescent tubes outside and on top of the box.

Fumigants (e.g. ozone and a hydrocarbon) were introduced into separate mixing tubes at the right end of the exposure box (Fig. 2). Each fumigant was diluted by a separate stream of carbon-filtered air before mixing. Thus when the reactants first encountered each other they were already at low concentrations, which ranged from 1 p.p.m. to 10 p.p.m. for ozone and from 1 p.p.m. to 35 p.p.m. for the olefin. HAAGEN-SMIT *et al.* (1952) reacted the materials at relatively high concentrations in a small reaction tube and then diluted the products to the desired concentration. Under these unrealistic conditions, a viscous polymer condensed on the reaction tube. CANN *et al.* (1954) also introduced ozone and gasoline or exhaust separately into a large chamber so that reactions occurred at low concentrations.

The mixed fumigants entered the infrared cell first and then passed across the plants and back into the cell. The air flow out of the cell (and therefore also into it) was regulated by changing the number of open bleed tubes at the left end of the cell. This air flow out of the cell was small compared to the main circulation through the cell and plant box, which was estimated to be several hundred liters per minute. Under these conditions the composition of the fumigation mixture should be uniform throughout the system even when chemical reactions are occurring. These are the defining

characteristics of a stirred flow reactor. The residence time is defined as the total volume of the system divided by the flow rate out of it.

Pinto bean *Phaseolus vulgaris L.* plants, 14 days old, were used as the test material for damage studies. These were chosen because ozone and oxidant damage can readily be distinguished on them—ozone inciting a spotty bleaching of the upper leaf surface while oxidant induces a glazing on the under side of the leaf. The plants were grown in an air-conditioned, carbon-filtered glasshouse at Riverside. Plants were transported to South Pasadena in an air-conditioned, carbon-filtered, illuminated box mounted on a pickup truck. Injury to the primary leaves of exposed plants was estimated on the second day after exposure as per cent of leaf surface damaged and recorded on an injury index scale of 0–10, wherein a value of 10 indicates 100 per cent injury. A given value is the average of the damage on a minimum of 30 leaves.

Unless otherwise stated, the fumigants were introduced and the system brought to a steady state before plants were placed in the exposure box. The concentration given for each component is that which would have been attained if no reaction had occurred.

EXPERIMENTAL RESULTS

Ozonides

The ozonides of 1-pentene and 2-pentene were prepared by bubbling ozonized oxygen through solutions of the corresponding olefins in liquefied petroleum gas at dry-ice temperature. Upon warming to room temperature the solvent and carbonyl impurities boiled off. Pinto beans showed no injury after a 2 hr exposure to an average concentration of 1-pentene ozonide of 3·5 p.p.m. Likewise, a 1 and 1½ hr exposure to 4·4 p.p.m. of 2-pentene ozonide failed to damage the pinto beans. These concentrations are far higher than could reasonably be expected to occur either in the atmosphere or in the experiments reported hereinafter. Therefore oxidant plant damage cannot be blamed either on the ozonides or on any hydrolysis or decomposition products of these quite stable materials.

Ozone–olefin mixtures

Haagen-Smit *et al.* (1952) demonstrated that 1-hexene was the most active olefin, of the several tested, for producing plant damage in ozone–olefin mixtures. Therefore, to establish a reference point in these experiments, the comparative activity of four ozone–olefin reactions, at comparable concentrations, was determined. The results are summarized in Table 1 and photographs of the damaged plants are shown in Fig. 3.

The 1-hexene–ozone reaction mixture produced the most damage while that from 3-heptene was almost as severe. Much less damage was produced in the 1-pentene experiment and none was caused by the 2-pentene–ozone mixture.

This result appeared to confirm the work of Haagen-Smit *et al.* (1952) who reported that the products of the 2-pentene–ozone reaction would not cause oxidant damage while many other olefins of similar structure were active in this respect. There was, however, one unusual aspect of the 2-pentene experiments. It was noticed that no ozone could be detected by means of the infrared spectrum when these rather large excesses of 2-pentene were added. This contrasted with the experiments with the other olefins in which a few tenths of a p.p.m. of ozone could be detected in the steady state

VO
1
1958

VOL.
1
958/9

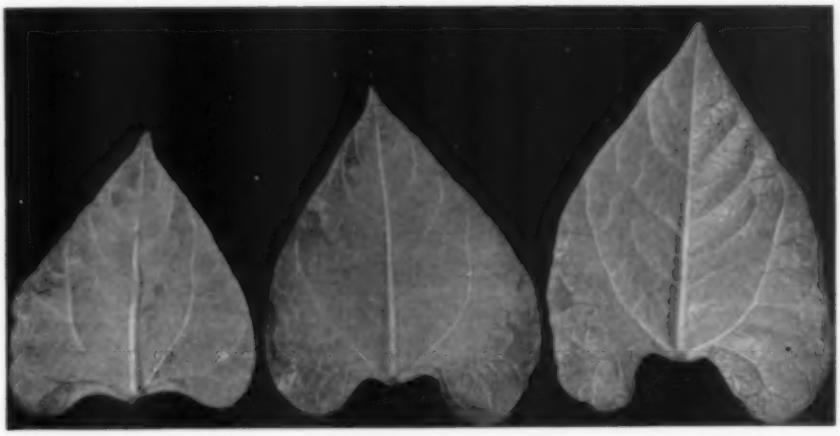


FIG. 3. Oxidant damage to pinto bean leaves from three ozone–olefin reactions at concentrations of 1 p.p.m. and 15 p.p.m. respectively: from left to right, 1-pentene, 3-heptene and 1-hexene.

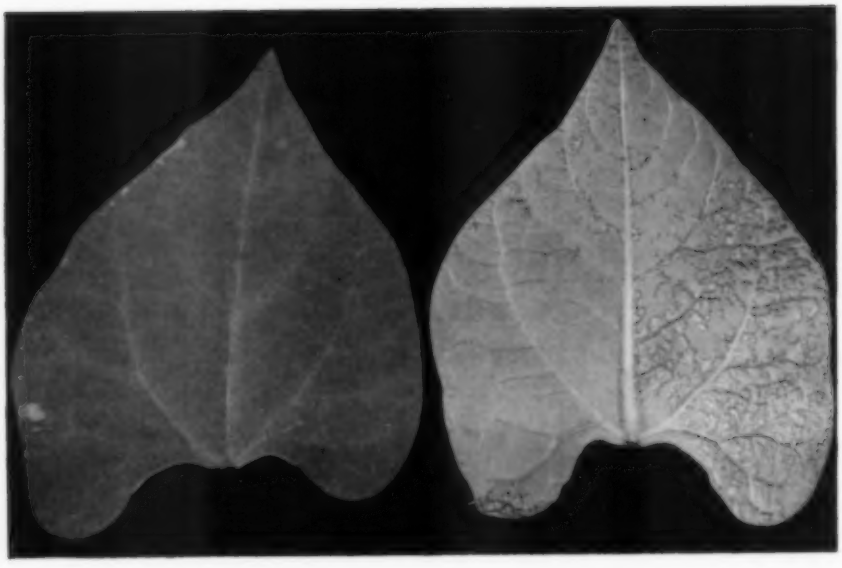


FIG. 4. Oxidant damage to pinto bean leaves from reaction of ozone with 2-pentene at concentrations of 10 p.p.m. and 15 p.p.m. respectively. Damage does not occur on upper surface (left) but is typically confined to the lower surface (right).

VOL
1
1958/

TABLE 1. DAMAGE TO PINTO BEAN PLANTS CAUSED BY EXPOSURE FOR 30 min TO REACTION OF OZONE WITH FOUR OLEFINS

Date and hr	Olefin	Concentration before reaction		Residence Time (min)	Injury index (Maximum = 10)	
		Olefin (p.p.m.)	Ozone (p.p.m.)		Oxidant	Ozone
19 March 1957						
1049	1-hexene	15	1	19	1·9	0·4
1151	2-pentene	15	1	19	0·0	0·0
1402	3-heptene	15	1	19	1·7	0·4
1501	1-pentene	15	1	19	0·9	0·2
14 March 1957						
1614	1-pentene	35	0·9	19	1·1	0·3
	2-pentene	10	2·0	19	0·0	0·0

reaction mixture. The ozone injury indexes given in the last column of Table 1 confirmed the fact that the ozone was completely consumed by the 2-pentene but not by any of the other olefins. Ozone injury occurs on the upper leaf surface in contrast to oxidant injury which occurs on the lower surface. Thus ozone injury can be estimated separately from oxidant injury on a single pinto bean leaf as shown by MIDDLETON *et al.* (1957).

The complete consumption of ozone by 2-pentene in the stirred flow system indicated that this olefin reacted appreciably faster than the other olefins that were tried. This was confirmed by subsequent measurements of the rates of these reactions. (Details of these rate studies will be published elsewhere.) This discovery suggested that the failure of 2-pentene–ozone mixtures to cause damage might be related to its unusually high reaction rate rather than to the difference in structure which, after all, is quite minor.

Furthermore, it was recognized that with this very fast reaction the system might no longer operate as a true stirred flow reactor, i.e. the concentrations of reactants and products might not be uniform throughout the system but might decrease continuously from the mixing point. Inasmuch as the mixture passed through the infrared cell before reaching the plants, it appeared possible that the plants were not exposed to an ozone-containing mixture when the ozone-2–pentene fumigations were carried out. Therefore a further series of fumigations was carried out with these mixtures. These are summarized in Table 2. When the ozone concentration (before reaction) was increased to 10 p.p.m. and the residence time decreased to 12 min, a 30 min fumigation produced strong oxidant damage as shown in Fig. 4. The actual ozone concentration could not be measured in these experiments because the salt windows of the infrared equipment were etched, but it must have been well below 1 p.p.m. since no ozone injury was observed on the plants. The next two experiments were done at reduced olefin concentrations and without recirculation of the fumigation mixtures, i.e. the mixture was passed through the cell, then over the plants, and then discarded. With these conditions the ozone was not completely consumed as indicated by the second value of concentration given in Table 2. In these experiments as well as in a 30 min stirred flow fumigation with 1 p.p.m. each of ozone and 2-pentene a slight amount of typical oxidant damage was obtained. These results clearly showed that the phytotoxicant *is a quite unstable species.*

Table 2. Effect of residence time and concentration on damage from ozone–2-pentene reactions

Concentration before reaction		Residence time (min)	Period of plant exposure (min)	Injury index (maximum = 10)	
2-pentene (p.p.m.)	Ozone (p.p.m.)			Oxidant	Ozone
2·0	1·0	19	60	0·0 (trace)	0·0
10·0*	2·0	19	30	0·0	0·0
15·0*	1·0	19	30	0·0	0·0
15·0	10·0†	12	30	3·8	0·0
15·0	10·0†	12	30	3·8	0·0
5·0	1·0 to 0·5	2‡	60	0·0	0·0
2·6	1·1 to 0·7	2‡	60	0·9	0·0
1·0	1·0	9	30	0·3	0·0
1·0	1·0	9	30	0·0	0·6

* Also reported in Table 1.

† Estimated.

‡ Straight through (i.e. no recirculation of fumigation mixture).

Failure to obtain damage from 2-pentene in the series of experiments with different olefins (Table 1) can only be explained by the formation and complete decomposition of the toxicant between the point of mixing and the plant exposure box.

Additional experiments were conducted with ozone and 1-pentene wherein the concentration of ozone was held constant and that of 1-pentene was varied. The results are given in Table 3.

Table 3. Plant damage from exposure for 30 min to ozone–1-pentene reactions at three concentrations of olefin

Concentration before reaction		Residence time (min)	Injury index (maximum = 10)	
1-pentene (p.p.m.)	Ozone (p.p.m.)		Oxidant	Ozone
3·2	0·9	19	0·9	0·7
17·5	0·9	19	2·2	0·7
35·0	0·9	19	1·1	0·3

Maximum damage occurred at a concentration of 17 p.p.m. of olefin and less damage occurred when this concentration was either decreased or increased. Instability of the phytotoxicant is also suggested by this result because the decreased damage at the higher olefin concentration can be explained by the more rapid consumption of ozone to form the phytotoxicant which then partly decomposes before reaching the plants.

Instability of the phytotoxicant

A few experiments were made to verify directly the instability of the phytotoxicant. In these experiments an ozone–1-hexene reaction mixture was brought to steady state in the dynamic system in the usual manner. A group of plants were then exposed for 30 min to obtain a reference of damage. At the end of the dynamic fumigation period, the plants were removed, the addition of ozone and 1-hexene was stopped, and the fresh-air intake was closed. A second set of plants was then fumigated either immedi-

ately or after a 30 min or 60 min delay by circulating this same sample over the plants. Damage to the second set of plants would demonstrate the continued presence or formation of the phytotoxicant.

Extensive damage was obtained in all reference experiments in the dynamic system. However, when the second set of plants was placed in the box, regardless of the interval between dynamic and quasistatic conditions, no plant damage occurred. This indicates that the life of the phytotoxicant is less than 30 min and perhaps much shorter. The small amount of ozone present at steady state in the dynamic system disappeared quickly, of course, when the inflow was stopped. The excess hexene remained unchanged throughout the quasistatic experiment. Experience with this system has been that most stable substances will remain unchanged in the air for long periods so that the toxicant probably was not absorbed on a surface. Studies of the stability of the phytotoxicant are continuing.

The fact that the phytotoxicant is unstable greatly increases the difficulty of unambiguously identifying it by long-path infrared or by any other means. On the other hand, all stable materials are ruled out by this observation.

Attention can also be drawn to the contrast with the studies of eye irritation carried out by Stanford Research Institute (FAITH *et al.* 1958). They found that the eye irritant produced by irradiating diluted automobile exhaust with artificial sunlight has a half life of many hours in the dark. It seems unlikely that the irritant is the same material which produced the oxidant injury to pinto beans. One is led to suspect the ozone–olefin addition complex or the zwitter ion which is formed subsequently and then decomposes (see earlier discussion). If a material could be found which would react with one or both of these materials it should act as a suppressant for plant damage.

VOL.
1
58/9

Addition of aldehyde to ozone–olefin reaction

Inasmuch as aldehyde apparently reacts with either the zwitter ion or the addition complex to form ozonide, it was suggested that excess aldehyde would prevent plant damage.

Paired experiments were made with ozone and 1-hexene and with ozone and 1-pentene wherein damage was obtained as a reference in the first experiment of the pair and an aldehyde was added to the reaction in the second experiment. Propylaldehyde was added to the ozone–1-hexene reaction and acetaldehyde to the ozone–1-pentene reaction. In both cases there was no reduction in damage when the aldehyde was added to the reaction, and the aldehyde apparently did not interfere with the activity of the phytotoxicant.

Unfortunately these experiments cannot be interpreted unambiguously as the extent to which the aldehyde enters the reaction is not known with certainty. Evidence was obtained in separate experiments that addition of excess aldehyde did increase the yield of ozonide and also changed the relative amounts of internal and terminal ozonides. Excess aldehyde did not, however, decrease the yield of ketene; a minor product attributed to the decomposition of the two-carbon zwitter ion:

$$CH_3 \cdot \overset{H}{\underset{|}{C}}—OO \rightarrow CH_2=C=O+H_2O$$

For the time being these experiments with added aldehyde must be regarded as inconclusive.

Addition of sulfur dioxide to ozone–olefin reactions

The addition of sulfur dioxide to nitrogen dioxide–gasoline reactions in sunlight has been reported to prevent plant damage. (Haagen-Smit *et al.* 1952). If it were found that sulfur dioxide could prevent oxidant damage from ozone–olefin reaction mixtures, it would provide a clue as to the nature of the toxic material. It appeared possible that sulfur dioxide had a protective effect as a reducing agent against the phytotoxic oxidant. Sulfur dioxide has since been shown to have no protective effect against ozone alone (Middleton *et al.* 1957).

Paired experiments were again made with ozone and 1-hexene wherein damage was obtained as a reference in the first experiment and sulfur dioxide at 0·5 p.p.m. was added to the reaction in the second experiment (Fig. 5). In two such pairs there was no effect of sulfur dioxide and oxidant damage was equally severe in each experiment pair.

SUMMARY

The reaction of ozone with olefins occurs sufficiently rapidly even at concentrations of a few parts per million to produce in a few minutes significant amounts of a substance capable of reproducing on pinto bean plants the oxidant injury observed in the Los Angeles area. Definite evidence was obtained that the toxic material is itself quite unstable even in the gas phase at extremely low concentration. This agrees with the experience that no pure substance is known which will produce these injury symptoms at these low concentrations; this list includes pure ozonides and formic acid as well as many aldehydes and other compounds. The instability of the phytotoxicant suggests that either an ozone–olefin addition complex or the zwitter ion into which it decomposes is responsible or perhaps both. Attempts to verify this by removing the toxicant with excess aldehyde or with sulfur dioxide were not successful.

Acknowledgement—The financial support of the Smoke and Fumes Committee of the American Petroleum Institute and the guidance of Project Advisory Committees VI and IX are deeply appreciated.

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VOL.
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958/9

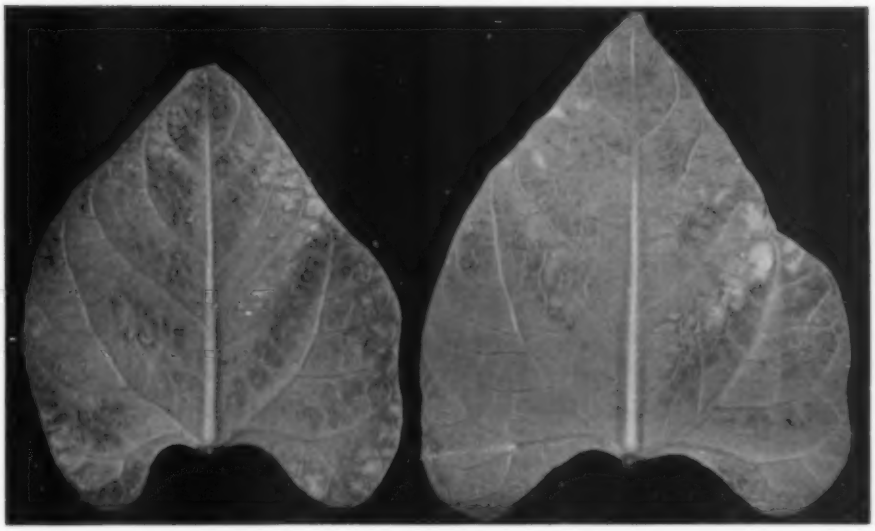

FIG. 5. Oxidant damage to pinto bean leaves fumigated with ozone-1-hexene (left) and with the addition of 0·5 p.p.m. of sulfur dioxide (right). The addition of sulfur dioxide did not prevent damage.

VO
1
1958

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APPLICATION OF MICRODIFFUSION OF ORGANIC ACIDS TO AIR ANALYSIS

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Abstract—Experiments were conducted to determine by microdiffusion techniques the effect of particulate materials on the escape of volatile organic acids from certain solutions. Since acetic and formic acids had been identified in atmospheric samples, radioactive samples of these materials were used as tracers in some of the experiments. The particulates were shown to affect the diffusion of the volatile organic acids.

INTRODUCTION

In a previous report (Marshall and Fox, 1958) a technique was presented for the characterization of organic acids by microdiffusion in Conway cells.

The microdiffusion approach is concerned with the rate of transfer of an acid from one area of a circular flat vessel to another area (of the same vessel) marked off by a circular wall concentric with but smaller than the vessel wall. The apparatus thus becomes one shallow circular vessel within another (Conway and Byrne 1933). The wall of the inner vessel is 1 mm beneath the top of the vessel when covered; in this way vapors or gases can be transferred from the one compartment to the other. Such an apparatus is called the Conway cell and is better known for its use in the microdetermination of ammonia. The cover for the vessel is a round plate having the same diameter as the outer diameter of the vessel. An air-tight seal results when the cover is placed on the greased edges of the vessel.

Both aqueous and nonaqueous solutions were evaluated as diffusion media. The behavior of the acids in aqueous media followed expectations in the light of the Duclaux constants for acid transfer by distillation.

The Duclaux constants (Shriner *et al.* 1956) are percentages of a volatile acid transferred at defined intervals on distillation under specified conditions. In general beginning with 100 ml of a 2 per cent solution of an acid, for example propionic, the first, second and third 10 ml quantities of the distillate are titrated; 11·9, 11·7 and 11·3 per cent of the initial acid will appear in the first, second and third 10 ml of the distillate. For formic acid corresponding values would be 3·95, 4·40 and 4·55 while for acetic acid such percentages transferred would be 6·8, 7·1 and 7·4.

In nonaqueous media the acid diffusion seemed less dependent on the quantity of solvent transferred. In addition, the rate of escape of an acid from nonaqueous media was influenced by other solutes present, unlike comparable transfer in aqueous media which even allowed the extension of the Duclaux behavior to mixtures. Consequently, like characterization by melting points, boiling points or related physical constants, qualitative identification of an acid by diffusion from nonaqueous media requires that the acid be in a high state of purity. Yet unlike the procedures for melting point and boiling point, the new microdiffusion approach does not require the acid to be free of solvent as long as the microdiffusion characteristics of the corresponding authentic acid can be evaluated in the solvent involved. This approach, however, means that the composition of the solvent vehicle must be known as the basic requirement. When the solvent vehicle is one that separates the acid solute from other

VOL.
1
958/9

solutes on a chromatographic column, the single requirement is met because the unknown acid can thereby be compared with authentic acid in a vehicle of identical composition. When complex mixtures such as air samples are analysed the agreement between the observed microdiffusion constants of the naturally occurring and authentic acid thus provides unequivocal identification of the acid. Chromatographic mobility becomes the supporting rather than the sole index for deciding the chemical nature of an acid separated from air by the chromatographic technique. Obviously, deviation of the microdiffusion constant of unknown and authentic acid indicates clearly that the chromatographic effluent is releasing solute(s) other than the one assigned to the *Rf* under scrutiny. Applications of this approach for the characterization of μg quantities of organic acids from the air particulate matter provide the basis for this report.

MATERIALS

Air particulate samples used were from Louisville air and were identified by filter numbers 2949, 15751, and 15752 of the National Air Sampling Network of the Community Air Pollution Program, U.S. Public Health Service.

Benzene extracts used for the " binding " experiments (explained below) were pooled from such extracts of Philadelphia particulate matter collected in April, May, and June, 1956.

Benzene extracts used for the countercurrent distribution studies were pooled aliquots of samples of particulate matter from urban air identified by numbers 15751 to 15757 by the National Air Sampling Network of the Community Air Pollution Program, U.S. Public Health Service.

PROCEDURE

Details of the procedure for microdiffusion have been previously reported (Marshall and Fox, 1958). This procedure, in general, involved placing $3 \pm 0{\cdot}5$ g sodium hydroxide pellets in the center well of a 7 cm diameter Conway cell (Microchemical Specialties). A scoop made from a portion of a 10 ml beaker delivered this quantity of dry pellets. A solution of the organic acid to be identified was placed in the outer vessel of the Conway apparatus. Acids having less than 4 carbons were characterized in nonaqueous solvents such as benzene, chloroform, *cyclo*hexane, heptane, or mixed solvents such as butanol–chloroform mixtures. Acids having more than 4 carbons were characterized in aqueous media but with Conway cells having a diameter of 2·5 cm. The cells of smaller diameter permitted diffusion periods no greater than 2 hr from aqueous media. The basis for characterizing an acid was essentially rate of escape from the outer vessel into the center well. Once the quantity of acid originally placed in the outer vessel was known (i.e. a " standard "), the amount of acid remaining after the diffusion period permitted the calculation of percentage acid remaining. Percentage of acid remaining in the Conway cell equaled:

$$\frac{\text{ml of 0·0015 N NaOH reqd. for Conway cell soln. after shaking/mass of sample added to cell}}{\text{(ml of 0·0015 N NaOH required for original solution/mass of original sample)}} \times 100$$

The value designated throughout as " percentage acid remaining " thus becomes the index for characterization of the unknown acid by microdiffusion.

Organic acids were leached from the air particulate by the use of 0·5 N sodium hydroxide. The extract was dried, acidified and mixed with silica gel and chloroform. The resulting slurry was placed on the silica gel column described below. Approximately 200 mg of particulate were adequate for analysis.

Chromatography followed the procedure of CORCORAN (1956). Gradient elution (DONALDSON *et al.*, 1952) employed a 500 ml mixing reservoir for the column into which butanol flowed. Thus the solvent for chromatography, initially chloroform, increased with respect to the concentration of butanol in chloroform. Three g silica gel columns were employed with an aqueous phase of 2 M glycine buffer pH 2. The effluent was fractionated automatically and alternate fractions were titrated with 0·0007 N sodium hydroxide in methanol containing 20 per cent (*v*/*v*) water and 20 mg bromthymol blue as the internal indicator. Alternate untitrated fractions for each acid were pooled and examined in the Conway apparatus to determine the microdiffusion characteristics. The vehicle delivering the acid solute from the column thus became the solvent for microdiffusion.

Since the microdiffusion characteristics of effluent acetic acid from air deviated from those of the comparable authentic acid, the behavior of the isolated two-carbon compound was re-examined with introduced radio-active carboxyl-labeled acetic acid. In the tracer experiments, labeled acids were counted as the sodium salts. Since the standard (i.e. sample before diffusion) was prepared in the same way as the sample after diffusion, no correction for absorption was necessary. Samples and standard were counted with an end window Geiger counter, the window thickness of which was less than 2 mg/cm^2.

VOL. 1 58/9

The radioactive tracers, H^{14}C OONa and $CH_3{}^{14}$C OONa, purchased from Tracerlab, had a specific activity of 1 mc/mmole each. In converting the sodium salt of the isotopic compound to the acid, 10–15 mg of the salt, 200 mg of silica and 0·2 ml of glycine buffer pH 2 were mixed. The resulting apparently dry mass was suspended in butanol–chloroform (4·06 per cent butanol in chloroform *v*/*v* for acetate and 8·63 per cent for formate). The resulting suspension was poured as a miniature chromatographic column and sufficient appropriate butanol–chloroform mixture was added so that the effluent had a volume of 50 ml. One ml of this solution was added to the unknown in corresponding butanol–chloroform solvent and examined in the Conway cell. The purpose of using tracers in studies of this type resides essentially in the increased sensitivity of the final means of detection of the acid through its radioactivity. In this way the effect being studied can be evaluated by a smaller amount of the introduced acid than would be possible with nonradioactive materials.

The microdiffusion procedure was applied to benzene extracts of particulate matter in two ways. In the first of these, the tracer dose was shaken in the Conway cell with benzene extract. The dry benzene extract was dissolved in chloroform and an aliquot of the solution containing 1–2 mg of the extract was dried in the outer vessel of the Conway apparatus. Into control cells was placed chloroform which was then evaporated in order to be certain that any tracer impurity from the chloroform appearing with the sample would likewise appear with the control. The solvent for the microdiffusion was 4·06 per cent butanol in chloroform (MARSHALL and FOX, 1958). The rate of escape of the H^{14}C OOH was determined by observing the radioactivity residing in the sodium formate on the surface of the sodium hydroxide pellets promptly at the end of the period of microdiffusion. The second application of microdiffusion

to the benzene extract of particulate matter involved the microdiffusion characteristics of a silica gel chromatographic fraction. This zone represented the acid found in the sodium hydroxide hydrolysate of the lower phase of a four-stage countercurrent distribution in the system chloroform–ethanol–heptane–water (2 : 1 : 1 : 1·3). In this distribution the upper and lower phases had a volume of 32 ml each.

Counter-current distribution is extraction by successive transfers. Consider, for example, two solutes *A* and *B* residing together in 10 ml of chloroform in a separatory funnel. If to this 10 ml of chloroform solution are added 10 ml of water and the mixture is shaken until there is equilibration of the solutes; the solutes will now have distributed themselves between the water (upper layer because the density is almost 1) and chloroform (lower layer because the density is about 1·5). The amount of *A* in the water layer and in the chloroform layer is often expressed as

$$\frac{C_A(H_2O)}{C_A(CHCl_3)} = K_1$$

and K_1 is called the distribution coefficient. In the strict sense the activities are the true thermodynamic functions rather than concentration, but concentration for dilute solutions is a frequently used approximation.

Similarly for *B*:

$$\frac{C_B(H_2O)}{C_B(CHCl_3)} = K_2$$

Thus the values of K_1 and K_2 would decide the separation of *A* and *B* that would result after equilibration in the first funnel. If we assume that 1g of each solute (*A* and *B*) was placed in the funnel and K_1 for *A* is equal to 2 while K_2 for $B=1$, then the upper phase of *A* will contain 0·66g of *A* while it contains 0·50 g *B*. This means that *A* is approximately 57 per cent pure. If we now transfer the upper phase of funnel one to a second funnel containing 10 ml pure chloroform and if we place pure water on top of the chloroform solution remaining in funnel one and shake the two funnels, the upper phase of funnel 2 would contain 0·44 g of *A* and 0·25 g of *B*. *A* is now approximately 63 per cent pure. If we transfer the upper phase of funnel 2 to pure chloroform in vessel 3, the upper phase of 1 to the lower phase now already in 2 and then place pure water on top of the lower phase already in 1, the upper phase of funnel 3 will be 70 per cent pure. Funnel 2 in both phases combined would contain 0·5 g of *B* and 0·44 g *A* while funnel 1 in both phases combined would contain 0·11 g *A* and 0·25 g *B* or *B* is almost 70 per cent pure in funnel 1. Obviously by increasing the number of stages (funnels) one can get *A* or *B* in a fair state of purity.

Countercurrent distribution, therefore, has a broader use than that given it in the text above. The countercurrent extraction is a means for characterizing chemical compounds as well as for studying their homogeneity. It has been shown that the mobility of a given solute in a series of funnels is such that when its total concentration in both phases of each funnel is plotted against funnel number the curve will approximate the Gaussian distribution. The position of the maximum of the curve as well as the symmetry are guides to the identity and purity of the chemical compound under investigation (Craig, 1944; Craig *et al.*, 1945; Williamson and Craig, 1947).

RESULTS AND DISCUSSION

The chromatographic system described above released solutes from the extract of air particulate in four distinct zones. When the titration values for the effluent fractions were plotted against fraction number, one irregular peak and four discrete peaks resulted. The first, between the 8th and 18th ml of effluent, was composed of acids having four or more carbons. The second, between ml 20 and 30 corresponds to acid or acids having the *Rf* of propionic acid. The general symmetry of the propionate zone as well as the absence of a discrete peak strongly suggested lack of homogeneity of this zone. Therefore, microdiffusion was not applied to the solutes

VOL 1 1958/

of this zone. The third zone, between 48 and 60 ml of effluent, was presumed to be acetic acid from the *Rf* of this acid. When alternate untitrated samples of this zone were pooled and studied for microdiffusion characteristics in the Conway apparatus, observed values for percentage acid remaining were 73·0 and 78·6. The value 73·9, compared to the previously observed mean values 86·2 (range, 2 analyses, 2·7), suggested contamination of acetic acid by other solute(s). The fourth chromatographic zone was presumed to be formic acid. When alternate fractions of this zone were pooled and analyzed in the Conway apparatus, two determinations showed 63·8 and 65·11 per cent acid remaining. These data compared sufficiently well with the value for the authentic acid, 65·11, that there could be no doubt that formic acid was a part of the extract of the 173 mg of particulate matter sample.

TABLE 1. DISTRIBUTION BY RADIOACTIVITY* AND TITRABLE ACIDITY OF FORMIC AND ACETIC ACIDS IN NONAQUEOUS SOLUTIONS IN CONWAY CELLS AFTER 2 hr AT 23°

Acid					Percentage acid remaining			
Sample (μg)		Radioactivity (counts/min 100 counts) ^{14}C-label*			Sample (μg)	Titrable acidity		
		Number of cells	Average (per cent)	Range		Number of cells	Average (per cent)	Range
Acetic	60	3	85·8	1·8	4×10^4	2†	86·2	2·7
	6	2	85·4	1·0				
Formic	25·9	3	54·9	6·6	4×10^4	2†	47·2	1·8
Effluent inert	197	3	77·2	5·5	197	3	70·0	2·7
Acetic + $CH_3{}^{14}C\,OOH$‡								

* ^{14}C-carboxyl labeled acids were employed. Counting details appear in the text.

† These values were taken from a previous report (MARSHALL and FOX, 1958).

‡ The radioactive acid was added after the emergence of the solute.

The data of Table 1 show the behavior of ^{14}C-labeled organic acids in Conway cells as determined by the measurement of radioactivity. The details of the temperature control are mentioned by MARSHALL and FOX (1958). Experiments employing nonaqueous solutions can very well be carried out in laboratories with standard air (conditioning) temperature control. The observed value for the smaller quantities (6, 24·9 and 60 μg) of the acids as compared to the larger (40 mg) quantities in the previous report illustrate that the rate of escape of the acid is independent of its initial concentration. The discrepancy between the distribution of effluent acetic and $CH_3{}^{14}C\,OOH$ in the Conway cell and the control illustrates that the chromatographic effluent containing acetic acid from particulate matter is not homogeneous. While the interfering material could be a polar compound other than one containing the carboxyl group, it is more probably an organic acid. The previous study pointed out that the rate of escape of an organic acid is more sensitive to acids than to alcohols (butanol at least) when either are in μg quantities.

The occurrence of volatile organic acids in particulate matter, suggested by TEBBENS and TORREY (1954) and shown by MADER *et al.* (1955) and our findings, suggests that the particulate matter is doubtless more representative of the total air sample than one would adduce from the chemical nature of known components of air and the process for

collecting the air particulate matter. This interpretation is based on the assumption that chemical compounds as well as carbon of particulate matter tend to prevent the escape of molecules ordinarily expected, because of vapor pressure or size, to remain with the air filtrate. Another application of microdiffusion analysis, a preliminary test of the degree to which compounds extracted from the air particulate interfere with the escape of radioactive formic acid, is shown in Table 2. It will be noted that the escape

Table 2. Influence of benzene extract of air particulate on the distribution of $H^{14}C$ OOH in Conway cells after 2 hr at 23°

Sample	Cell Number	Acid escaping (Observed counts over center well)
Control	1	501
	2	519
	3	496
Extract	1	380
	2	363
	3	377

of ^{14}C formate in the controls is greater than that in the cells containing the extract of the particulate. It should be emphasized that the observations shown are relative values. The observed counts were obtained by counting the radioactive formate retained on the sodium hydroxide pellets *promptly at the end of the period* of microdiffusion. They do not provide a basis for calculation of percentage acid remaining

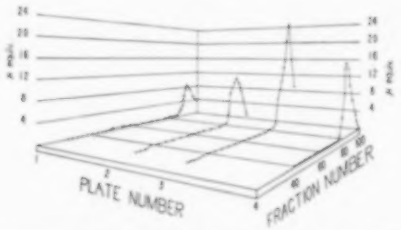

Fig. 1. Chromatographic representation of acid released by alkaline hydrolysis of the lower phase of a four-stage countercurrent distribution of 32 mg of benzene extract of particulate matter from urban air.

because a standard (i.e. zero diffusion time) having comparable geometry, absorption and related factors would be near unattainable. Obviously, converting the sodium formate and the standard to comparable samples for counting would permit the determination of percentage acid remaining and such preparations are being made in studies now in progress.

The data in Fig. 1 represent four chromatograms of the esterified acid of the lower phase of a four-stage countercurrent extraction of 32 mg of benzene extract representing 480 mg of air particulate matter. It will be noted that the greater part of the acidity in each case resides between chromatographic fractions 80 and 100. These data do not mean that no other ester-bound acid exists in the extract, but they indicate that

the other esters are doubtless lost on drying the extract or that the other compounds having the ester bond are so numerous that each exists in a concentration not measurable when the size of the extract sample is 32 mg. When the acidified portion of the chromatogram was tested for microdiffusion, the acid did not have the diffusion characteristics of formic acid even though its chromatographic mobility could have been mistaken for that of the 1 carbon acid. Four determinations in the Conway cell using 8·63 (MARSHALL and FOX, 1958) per cent butanol as the diffusion medium showed acid percentage remaining between 99 and 100. Thus a new acid or ester apparently results during the preparation of the benzene extract, or the acid or ester is not extracted from the particulate by this treatment. It seems unlikely that the latter explanation would suffice since the quantities of acid represented in the 32 mg of the 4 lower stages are 640 microequivalents. Since the maximum amount appears at stage 3, the distribution coefficient of the compound(s) must be greater than 1 (CRAIG, 1944, CRAIG *et al.*, 1945 and WILLIAMSON, 1947) indicating that there must be more acid in the upper phase of the solvent system. The amount of acidity in this region of the chromatogram obtained by hydrolyzing 480 mg of particulate would be 26 μ equiv. These observations mean that the acid in the extract is found in 50 times the amount found in the particulate. It is thus unlikely that hydrolyzing the particulate for the same length of time would provide only 2 per cent of the compound there. The implications of these findings are now under further investigation.

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VOL.
1
58/9

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THE PHYSIOLOGICAL RESPONSE OF GUINEA PIGS TO ATMOSPHERIC POLLUTANTS*

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Abstract—Changes in the mechanical behavior of the lungs were produced by 1 hr exposure of guinea pigs to low concentrations of irritant air pollutants. Sulfur dioxide, acetic acid, formaldehyde, formic acid and 0·8 μ sulfuric acid produced bronchial constriction, whereas 2·5 μ sulfuric acid resulted in obstruction of some of the larger air passages.

As evaluated by the increase in pulmonary flow-resistance and the increase in work of respiration the most potent of the gaseous irritants was formic acid, followed by formaldehyde, acetic acid, and sulfur dioxide in that order.

Extension of the exposure time indicated that the response to sulfur dioxide continued to increase during a 3 hr exposure, whereas prolonging the formaldehyde exposure to 4 hr indicated that the maximum response was produced in 1 hr.

In the case of sulfur dioxide, acetic acid, and formaldehyde the response was greater when the gases were breathed through a tracheal cannula, thus by-passing the scrubbing effect of the upper respiratory tract.

Using mixtures of sulfur dioxide and sulfuric acid mist, a synergistic toxic action was observed when the sulfuric acid particle size was 0·8 μ but not when 2·5 μ sulfuric acid was used. A potentiation of the response to sulfur dioxide was obtained with sodium chloride aerosol of 0·04 μ but not with 2·5 μ, hence particle size appears to be an important factor in the potentiation of the response to irritant gases by aerosols. The possible reasons for this are discussed.

When the four irritant gases used were studied in combination with 10 mg/m^3 sodium chloride of 0·04 μ diameter which was itself without effect on the animals, the response to sulfur dioxide and to formaldehyde was potentiated but the response to acetic and formic acids was unchanged. The aerosol, however, prolonged the response after the termination of the exposure in the case of all four gases.

The response to the combination of formaldehyde plus aerosol was greater than the response to the gas alone breathed through a tracheal cannula. The presence of a tracheal cannula used with the gas–aerosol mixture produced an increase exactly accounted for on the basis of the gas alone. At a given concentration of formaldehyde the response produced varied with the aerosol concentration. These experiments indicate that the increase of toxicity of a gas–aerosol mixture can be definitely related to the aerosol entity.

INTRODUCTION

EXTRAPOLATION of toxicological data obtained on experimental animals to the ultimate goal of setting safe levels for human exposure is at best beset with many difficulties. When the results are to be applied to air pollution, the gap is wide indeed between the low concentrations occurring even during periods of prolonged meteorological inversion over heavily polluted urban areas and the high concentrations necessary to produce lung damage and mortality in experimental animals. With this in mind, a means was sought for quantitative measurement of the response of

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experimental animals to concentrations of irritants below the levels required to produce gross signs of respiratory distress.

Methods were developed for measuring the mechanics of respiration in unanesthetized guinea pigs for periods of several hours. Changes in pulmonary flow-resistance and compliance indicative of bronchial constriction were observed during exposures of one hour to concentrations of the order of magnitude of those occurring during episodes of acute air pollution. The per cent increase in pulmonary flow-resistance is related to the concentration of irritant present. This fact permits the construction of dose-response curves which can be used to compare the response to various irritants alone or in combination with inert aerosols over a range of concentrations from below 1 p.p.m. to several hundred p.p.m. Data obtained thus far indicate that in several instances the effects of very low concentrations would not have been predicted correctly from data obtained only on high concentrations.

No attempt is made to predict the probable response of man from the data obtained with the guinea pig. The same data on mechanics of respiration can, however, be obtained on human subjects. If this were done during exposures to irritants, the response of the animals and man could be compared directly.

Four irritant gases (sulfur dioxide, acetic acid, formaldehyde, and formic acid) have been studied alone and in combination with a sub-micron particle size aerosol of sodium chloride which alone produced no response. Sulfuric acid mist was studied at three different particle sizes, 0·8, 2·5, and 7 μ. Sulfur dioxide was studied in combination with sulfuric acid mist of 0·8 and 2·5 μ to test for possible synergistic effects.

VOL.
1
58/9

METHODS

The physiological techniques developed for studying the mechanics of respiration on the guinea pigs have been published in detail (AMDUR and MEAD, 1958). Three measurements are necessary, intrapleural pressure, tidal volume, and the rate of flow of gas in and out of the respiratory system. Intrapleural pressure is measured by means of a fluid filled catheter inserted into the chest cavity. Tidal volume is measured by recording the pressure changes produced in a body plethysmograph. The rate of flow of gas in and out of the respiratory system is obtained by electrical differentiation of the volume signal with respect to time. Simultaneous tracings of these three measurements are made.

Intrapleural pressure has a resistive component which relates to resistance to flow of gas in the lungs and airway and an elastic component which relates to elastic recoil of the lungs. By relating the volume and flow-rate changes to intrapleural pressure changes at specific points during the respiratory cycle, these two components can be evaluated separately. The pulmonary flow-resistance is expressed in cm H_2O/ml/sec and the compliance, which relates to the elastic recoil, is expressed in ml/cm H_2O. A decrease in compliance indicates that the lungs are behaving as a less elastic system.

In the experimental design used, respiratory measurements were made every 5 min during a control period of $\frac{1}{2}$ hr, then the substance under study was added to the airstream of the exposure chamber for 1 hr, during which period respiratory tracings were again taken every 5 min. Post-exposure periods varied from 1 to 3 hr.

For establishing the concentrations of the various irritants, a dynamic exposure

chamber was used. In all cases the concentration of irritant present was determined analytically during the exposure period.

As described previously by AMDUR and MEAD (1955) and AMDUR (1957), the sulfur dioxide concentration was established by metering 1% sulfur dioxide in air from a cylinder into the main air stream. The air sample was collected in hydrogen peroxide–sulfuric acid reagent and the increase in conductivity was measured.

Acetic acid and formaldehyde vapors were generated by passing air through glacial acetic acid or 37% formaldehyde in a sintered glass bubbler. Formic acid vapor was generated by passing air over constant boiling formic acid in a flask. Air samples were collected in demineralized water. Acetic and formic acids were measured by increase in conductivity. Formaldehyde was measured colorimetrically with Schiff's reagent as recommended by ELKINS (1950) for concentrations above 1 p.p.m. and by the chromotropic acid method of MACDONALD (1954) for lower concentrations.

As described by AMDUR *et al.* (1952) and AMDUR (1958), sulfuric acid mist was generated by passing air through a heated flask containing concentrated sulfuric acid. Air samples were collected on a type HA millipore filter, the filter was soaked in demineralized water, and the conductivity of the resultant solution was measured. Cascade impactor sampling and the chemical method of MAY (1945) were used for routine particle size determination.

The sodium chloride aerosol was generated by aerosolizing a 1% sodium chloride solution in a Dautrebande generator (DELAUNOIS *et al.* 1956). Sizing from electron photomicrographs showed a mean size of 0·04 μ (σ 3·3).* For determination of the concentration, the aerosol was collected on a millipore filter, the filter was soaked in demineralized water and the resultant increase in conductivity was measured. When the aerosol was used in combination with an irritant gas, the filter preceded the midget impinger used for gas sampling.

RESULTS AND DISCUSSION

A. *Individual irritants*

The response produced in 1 hr by essentially equal concentrations of the five irritants tested is shown in Fig. 1. In order of increasing potency they are sulfur

TABLE 1

Irritant	Concentration used (p.p.m.)	Threshold limit (p.p.m.)
Sulfur dioxide	2·6	5
Acetic acid	5·0	10
Formaldehyde	3·5	5
Formic acid	2·8	None given
Sulfuric acid	3·6 (15·4 mg/m³)	0·25 (1 mg/m³)

* In a previous publication (AMDUR 1957) the electron microscope sizing data were not yet available so an attempt was made on sizing with the modified cascade impactor. This yielded a MMD of 0·2 μ. The figure of 0·04 μ is closer to specifications given by Dautrebande for the generator used. At the relative humidity of the exposure chamber (50 per cent) the particles were probably liquid droplets and would certainly have become so following inhalation.

dioxide, acetic acid, formaldehyde, formic acid, and sulfuric acid. Table 1, showing the concentrations used in Fig. 1 and the threshold limit values recommended by the American Conference of Governmental Industrial Hygienists (1957), may help in setting a frame of reference for the practical order of magnitude of the concentrations.

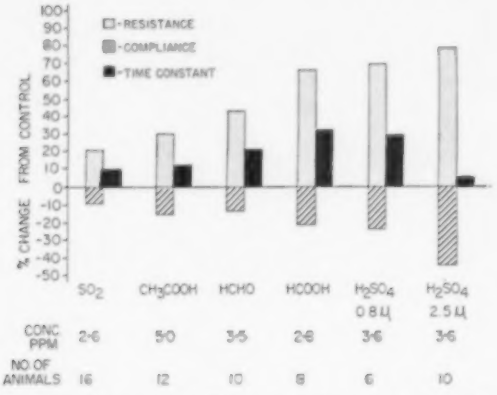

FIG. 1. Per cent changes in resistance, compliance, and time constant produced by 1 hr exposure to different irritants at concentration of 3 to 5 p.p.m.

The sulfuric acid concentration, chosen to be equivalent to the other irritants, is far above that which would normally be encountered. Concentrations close to the threshold limit value were tested, however, and 1·9 mg/m³ (0·5 p.p.m.) produced a 50 per cent increase in resistance (AMDUR 1958).

In each case the irritant produced an increase in resistance accompanied by a decrease in compliance. The product of the resistance (cm H_2O/ml/sec) and the compliance (ml/cm H_2O) has the unit of time and is known as the time constant of the lungs. In the case of narrowing of the air passages of the lungs due to bronchial constriction, the increase in resistance is proportionately greater than the decrease in compliance and the time constant of the lungs is elevated. Figure 1 shows that in the case of the four gaseous irritants and the 0·8 μ sulfuric acid the time constant is elevated. This suggests bronchial constriction as the physiological response to these substances.

In the case of the 2·5 μ sulfuric acid, the compliance decrease is proportionately greater, hence the time constant does not increase. Such mechanical behavior of the lungs is consistent with complete rather than partial obstruction of the air passages. (For example, if the major bronchus leading to one lung were totally obstructed, the compliance measured would be cut approximately in half, the resistance would be approximately doubled, and the time constant would remain unchanged.)

The appearance of the lungs post mortem and the fact that the response is delayed in time combine with the mechanical behavior of the lungs to suggest that the 2·5 μ sulfuric acid particles act by a different mechanism than the gaseous irritants and the 0·8 μ sulfuric acid (AMDUR 1958). Data in the literature on the site of deposition of aerosols of various particle sizes suggest that the 2·5 μ particles would have their major action at the level of the main bronchi rather than in the more peripheral portions of the lung as would the gaseous irritants and the sub-micron sulfuric acid.

VOL. 1 58/9

Sulfuric acid mist of 7 μ particles had very little effect on the animals at a concentration of 30 mg/m³. This would be expected as the particles of this size would be unlikely to penetrate beyond the upper respiratory tract.

The dose–response curves for the four gaseous irritants are shown in Fig. 2. These were obtained by plotting the per cent increase over the control value produced in pulmonary flow-resistance by a 1 hr exposure against the concentration of irritant expressed in p.p.m. The numbers beside each point indicate the number of animals

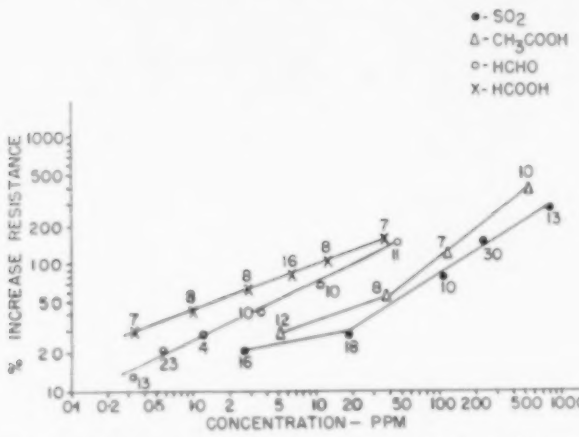

FIG. 2. Dose–response curves comparing four irritant gases. Per cent increase in resistance at the end of 1 hr exposure is the criterion of response and the concentration is expressed as p.p.m. by volume. The numbers beside each point indicate the number of animals used.

exposed at that concentration. In all cases the increase in resistance was statistically significant. Throughout the concentrations tested, formic acid was the most potent of the irritants, followed by formaldehyde, acetic acid, and sulfur dioxide in that order.

Examination of Fig. 2 shows that for sulfur dioxide and acetic acid the response to the low concentrations (2 and 5 p.p.m. respectively) is greater than would have been predicted had the curves been extrapolated from higher concentrations. Formaldehyde, on the other hand, behaves as would have been predicted. The explanation for the difference in behavior is not clear. The suggestion has been made that stimulation of the upper respiratory tract alone may produce reflex bronchial constriction. A trace of formaldehyde tends to deaden at least the sensory response to odors. Thus it is possible that if the response to low concentrations of sulfur dioxide or acetic acid results mainly from upper respiratory stimulation, this phenomenon is eliminated in the case of formaldehyde.

Another difference in behavior between sulfur dioxide and formaldehyde is shown in Fig. 3, which shows the results obtained in a 3 hr exposure of six animals to 24 p.p.m. sulfur dioxide and a 4 hr exposure of three animals to 50 p.p.m. formaldehyde. The resistance increase produced by the sulfur dioxide progresses from 20 per cent at the end of the first hour to 86 per cent at the end of the third hour. Three hours after the end of the exposure the resistance had returned to control levels. The resistance increase produced by the formaldehyde reaches its maximum by the end

of the first hour of exposure, drops slightly during the second hour, and then remains essentially constant during the remaining 2 hr of exposure. Two hours after the end of the exposure, the resistance had decreased markedly but had not yet returned to control values. These experiments were not done at comparable concentrations

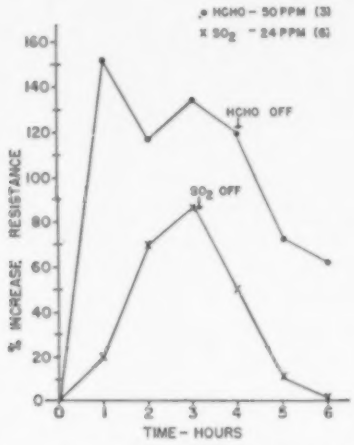

FIG. 3. Comparison of the response to a 3 hr exposure to sulfur dioxide with the response to a 4 hr exposure to formaldehyde.

of the two irritants; however, the results suggest that sulfur dioxide may produce a more cumulative type of response than does formaldehyde.

An estimate of the elastic and resistive work done in ventilating the lungs can be made from the data obtained on compliance, resistance, tidal volume, and frequency (OTIS *et al.* 1950). An increase in respiratory work has been a consistent finding for

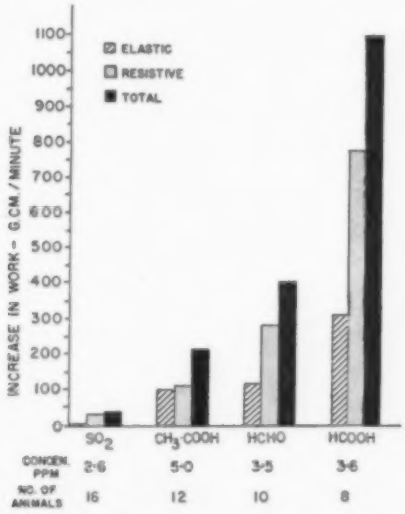

FIG. 4. Increase in elastic, resistive, and total work of respiration produced by a 1 hr exposure to different irritant gases at concentrations of 3 to 5 p.p.m.

all the irritants so far tested, even at low concentrations. Figure 4 shows the increase in elastic, resistive, and total work produced by low concentrations of the four gaseous irritants. Again formic acid is the most potent followed by formaldehyde, acetic acid, and sulfur dioxide. An increase of 1,100 g-cm/min in total respiratory work represents an approximate doubling of the control values for the guinea pig. Changes in respiratory work of this order of magnitude cannot *per se* be construed as constituting a major stress, and furthermore, the method of calculation yields only approximate values. As one of the responses to irritants, however, it might be kept in mind for future consideration from the point of view of a stress superimposed upon existing respiratory impairment.

In the case of a soluble gas a considerable amount may be removed during passage through the upper respiratory tract thus reducing the amount of irritant gas actually reaching the lungs at a given atmospheric concentration. LABELLE *et al.* (1955) suggested that this factor may be important in the potentiation of the response to irritant gases by inert aerosols. By inserting a cannula in the trachea, the scrubbing effect of the upper airway may be by-passed permitting a study of the response to a given atmospheric concentration reaching the lungs more directly. This was done for groups of animals exposed to sulfur dioxide, acetic acid, and formaldehyde.

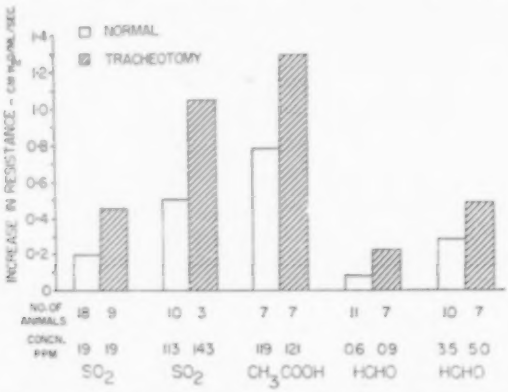

FIG. 5. Comparison of response of normal and tracheotomized animals to sulfur dioxide, acetic acid, and formaldehyde.

Figure 5 compares the resistance increase produced by a 1 hr exposure in normal and tracheotomized animals. With all three gases a greater response was obtained at a given atmospheric concentration when the protective effect of the upper airway was eliminated.

B. *Mixtures of gases and aerosols*

The first gas–aerosol combination studied was a mixture of sulfur dioxide and sulfuric acid mist. In this case both components of the mixture are irritant. The experimental design therefore involved determining a concentration of either alone which produced essentially the same increase in resistance. The response to a mixture of these two was then measured and compared statistically with the measured response to twice the concentration of either component alone.

The results of these experiments have been reported in detail (AMDUR 1957). When

the particle size of the sulfuric acid mist was 0·8 μ, the response to the mixture was greater than the response to the higher level of either constituent alone indicating a synergistic toxic action. When 2·5 μ sulfuric acid mist was used as the aerosol, the response of the mixture was not greater than the response to the higher levels of either constituent alone and was even slightly less than the response to the higher levels of sulfur dioxide.

The fact that the combination of the smaller sulfuric acid particles and the gas produces a response that is more than additive whereas the larger particles do not, may have several explanations. If one postulates adsorption of the gas on the aerosol particles, then from a purely physical viewpoint the larger particles would have proportionately less surface area and hence would carry less gas. In addition to this the percentage and depth of penetration of the particles into the lungs would be greater in the case of the smaller particles. As was indicated above and discussed more fully by AMDUR (1958), the smaller sulfuric acid particles appear to have a physiological action similar to that of sulfur dioxide, whereas the larger particles have their main site of action at the level of the main bronchi.

The question then arose whether or not an inert aerosol would affect the response to sulfur dioxide. An aerosol of sodium chloride at a concentration of 18 mg/m^3 administered alone for 1 hr had no detectable effect on the respiration of the animals. For most of the work with mixtures of gases and sodium chloride a concentration of about 10 mg/m^3 was used. Figure 6 shows the effect of a sodium chloride aerosol

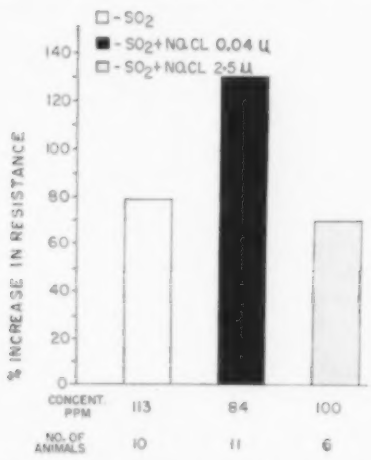

FIG. 6. Effect of 0·04 and 2·5 μ sodium chloride on response to sulfur dioxide.

of 0·04 μ and of 2·5 μ on the response to sulfur dioxide. The situation is similar to that seen with sulfuric acid mist in that the response is potentiated by the sub-micron particle size aerosol but not by the larger particles. The physical factor of different specific surface area and the physiological factor of percentage and depth of penetration must both contribute to the difference in behavior of the large and small particle size aerosols. Further gas–aerosol work was done in using the smaller sized particles only.

The details of the effect of an aerosol of sodium chloride on the response to sulfur

VOL. 1 58/9

dioxide were reported in a previous publication (AMDUR, 1957). Over the entire range of concentrations used from 2 to 200 p.p.m. sulfur dioxide the response was greater in the presence of the aerosol. Since dose–response curves were available for the gas alone and for the gas plus the aerosol, it was possible to compare the two on the basis of concentrations which produced an equal response. When this was

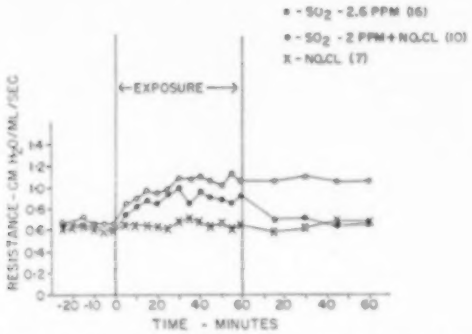

FIG. 7. Time course of the resistance change produced by sulfur dioxide alone and in combination with 10 mg/m³ sodium chloride. The control exposure to sodium chloride alone is also shown. The numbers indicate the number of animals exposed.

done it was found that at the higher concentrations ranging from 25 to 200 p.p.m. of sulfur dioxide, the response in the presence of the aerosol was equivalent to the response produced by approximately three to four times that concentration of gas alone. At low concentrations, this relationship no longer held and the response of 2 p.p.m. sulfur dioxide plus the aerosol was the same as the response to 70 p.p.m.

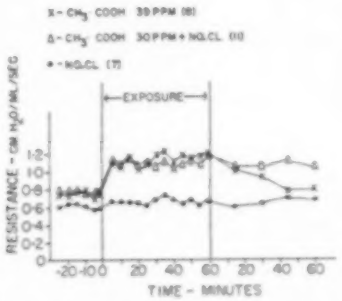

FIG. 8. Time course of the resistance change produced by acetic acid alone and in combination with 10 mg/m³ sodium chloride. The control exposure to sodium chloride alone is also shown. The numbers indicate the number of animals used.

gas alone instead of to 6 or 8 p.p.m. as would have been predicted on the basis of data obtained at the higher concentrations. In this instance again, the data obtained by actual experimentation at the low concentrations were different than would have been predicted from data obtained only on high concentrations. This fact may have practical importance in the planning of experimental work in air pollution toxicology.

The presence of the aerosol not only increases the degree of response to a given concentration of sulfur dioxide but also affects the duration of the response after

the exposure has ended. In Fig. 7 the course of the resistance with time is shown for a group of animals exposed to 2 p.p.m. sulfur dioxide alone and in the presence of 10 mg/m³ sodium chloride. The curve for animals exposed to sodium chloride alone is also shown. As was indicated above, this aerosol alone had no effect upon the respiration of the animals. The animals receiving 2 p.p.m. sulfur dioxide alone had returned to control resistance values by the end of 1 hr after the exposure, whereas those receiving the combination still continued to show an increased resistance.

A similar plot of the course of the resistance with time is shown in Fig. 8 for animals exposed to acetic acid alone and to acetic acid plus the sodium chloride aerosol. In this case the response to the combination and to the gas alone is essentially the same, hence the response to acetic acid has not been potentiated by the aerosol as was the response to sulfur dioxide and in this regard the two gases are different. The presence of the aerosol has, however, prolonged the response and in this regard the two gases are similar.

LABELLE *et al.* (1955) suggest that soluble gases which are normally partially removed during their passage through the upper airway are potentiated by the presence of an aerosol since this increases the amount of gas reaching the lungs. Acetic acid is such a soluble gas and, as was shown in Fig. 5, the effect is greater when the upper respiratory tract is by-passed with a tracheal cannula. If this theory were correct then one would predict that acetic acid would be potentiated by the aerosol as was the sulfur dioxide, but this is not the case.

If, of course, the acetic acid were not adsorbed on the aerosol then there would be no potentiation. On the other hand, the response to the combination continues after the exposure ends. This suggests that some interaction between the gas and aerosol has occurred. Before further discussion of the difference and similarity in the behavior of sulfur dioxide and acetic acid in the presence of the aerosol, the behavior of the other two gases, formaldehyde and formic acid, will be discussed.

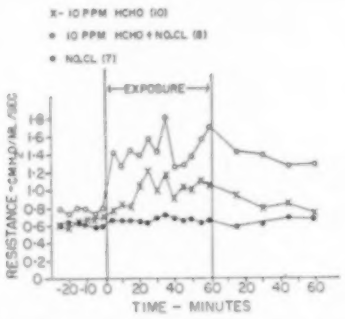

FIG. 9. Time course of the resistance change produced by formaldehyde alone and in combination with 10 mg/m³ sodium chloride. The control exposure to sodium chloride alone is also shown.

The course of resistance with time is shown in Fig. 9 for a group of animals exposed to 10 p.p.m. formaldehyde alone and plus 10 mg/m³ sodium chloride. The response is greater in the presence of the aerosol and continues after the exposure ends whereas the response to the gas alone has been completely reversible. Formaldehyde thus behaves as does sulfur dioxide. In Fig. 10 are shown the dose–response curves for

formaldehyde alone and in the presence of 10 mg/m³ sodium chloride. At all the concentrations tested from 0·3 to 50 p.p.m., the response was greater in the presence of the aerosol. These findings confirm the finding of LABELLE *et al.* (1955) that formaldehyde was more toxic in the presence of inert aerosols.

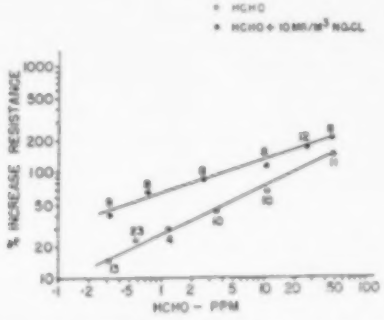

FIG. 10. Dose-response curves for formaldehyde alone and in the presence of 10 mg/m³ sodium chloride. Per cent increase in resistance at the end of 1 hr exposure is the criterion of response and the concentration is expressed as parts per million by volume. The numbers beside each point indicate the number of animals used.

The course of resistance with time for formic acid alone and in the presence of the sodium chloride aerosol is shown in Fig. 11. In this case the behavior is similar to that seen with acetic acid. The actual response is not potentiated but the response is prolonged.

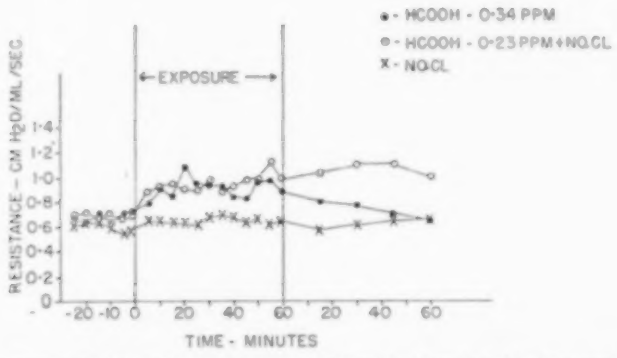

FIG. 11. Time course of the resistance change produced by formic acid alone and in combination with 10 mg/m³ sodium chloride. The control exposure to sodium chloride alone is also shown.

Of the four gases tested with the 10 mg/m³ concentration of sodium chloride two, sulfur dioxide and formaldehyde, were potentiated and two, acetic acid and formic acid, were not. With all four gases, however, the presence of the aerosol prolonged the response. The entire explanation for this pattern of events is not yet clear, but several things come to mind.

To explain the differences it is possible to consider the fact that *if* sulfur dioxide were oxidized to sulfuric acid, the result would be a more toxic product and *if* formaldehyde were oxidized to formic acid, the result would be a more toxic product.

On the other hand, oxidation of acetic or formic acid would not yield a more toxic product. LaBelle *et al.* (1955) found that nitric acid was not potentiated and in this case again chemical change would not yield a more toxic product. Thus none of the existing toxicological evidence conflicts with the theory that oxidation to a more toxic product plays a role in determining whether or not the response to an irritant gas is potentiated by an inert aerosol.

On the other hand, there is evidence that the presence of heavy metals to catalyze the oxidation is necessary for the conversion of sulfur dioxide to sulfuric acid and that such a reaction would be unlikely to occur on an aerosol of chemically pure sodium chloride such as was used in these experiments (Johnstone and Coughanowr, 1957; Gerhard and Johnstone, 1955; Johnstone, 1957). Furthermore the data obtained with formaldehyde seem explicable by a mechanism involving surface accumulation of the gas on the particles suggested to the author by Goetz which in no way involves oxidation.* This leaves the other obvious consideration of difference in physical properties. Formaldehyde and sulfur dioxides are gases, whereas acetic, formic, and nitric acids are liquids and have a higher boiling point. Such factors could materially influence the behavior of a gas–aerosol system and may possibly contribute to the differences observed.

The prolongation of the response noted in the case of all four gases is most likely related to the retention of the aerosol particles. Morrow and Gibb (1958) found that approximately 66 per cent of an aerosol of sodium chloride of 0·06 μ was retained in the dog. Thus, when the aerosol carries an irritant gas it seems reasonable that the response would continue even after the actual exposure had ended, even in the case of a gas in which the response during the exposure was not greater than that to the gas alone.

VOL.
1
58/9

Although there has been only a small amount of experimental work done in the field of toxicology of gas–aerosol mixtures, there has been no similar dearth of speculation—mostly as a result of the acute air pollution incidents. One suggestion made by Vorwald (1952) is that the inert aerosol carrying irritant gas is deposited on the lung tissue, thus setting up a high *local* concentration of irritant. If this reasonable suggestion is correct, then two things should follow both of which should yield to experimental proof with the present methods. First of all, the important factor in the potentiation of an irritant gas by an inert aerosol *would not be the increase in the actual amount of irritant gas reaching the lungs, but the fact that even a small amount of irritant reaches the lungs carried on the aerosol. Secondly, any increase seen in toxicity should be directly related to the aerosol entity.*

The first point should be clarified by comparing the response of animals exposed to the gas alone breathed through a tracheotomy so that more gas actually reaches the lung with the response of animals breathing the gas–aerosol combination. In Fig. 12 the results of such experiments using formaldehyde as the irritant and 10 mg/m^3 of sodium chloride as the aerosol are shown. At both 1 and 3·5 p.p.m., the response is greater when the upper airway is by-passed as was indicated earlier. The response, however, is *not* as great as when the gas–aerosol combination is given. This indicates that the important factor is that the gas is carried by the aerosol.

* The details of this mechanism will be published by Dr. Goetz simultaneously with the detailed data on the physiological effects of formaldehyde plus the aerosol.

The response to the gas–aerosol combination breathed through the tracheal cannula is also shown in Fig. 12. In this case, the response is again greater than that of the animals breathing the combination normally. The increase, however, is almost exactly what would be accounted for on the basis of increased transfer of gas

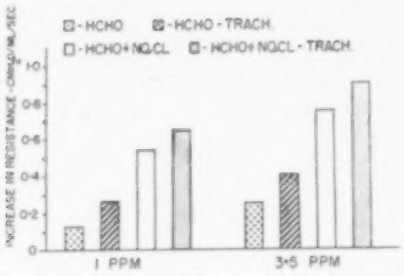

FIG. 12. Comparison of response of normal and tracheotomized animals to formaldehyde alone and in the presence of 10 mg/m³ sodium chloride.

alone. (In other words, gas + aerosol through tracheotomy – gas + aerosol breathed normally = gas alone through tracheotomy – gas alone breathed normally.) An aerosol of 0·04 μ will pass through the upper respiratory tract completely, hence the cannulation of the trachea should make no difference in the amount of aerosol reaching the lungs. The outcome of these experiments suggests very strongly that the increase in response is related to the aerosol entity as such.

Further evidence for this is presented in Fig. 13 which shows the effect of varying the aerosol concentration in the presence of the same concentration of formaldehyde.

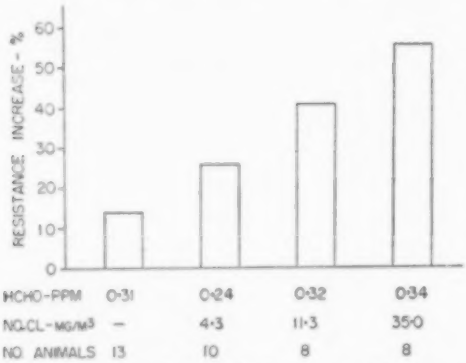

FIG. 13. Resistance increase produced by formaldehyde alone and in the presence of three concentrations of sodium chloride.

As the aerosol concentration was increased from 4 to 11 to 35 mg/m³ the response also increased. The obvious control of exposing animals to the sodium chloride alone at 35 to 40 mg/m³ was done and the aerosol alone at the higher concentration was without any detectable effect on the animals. The fact that the response varies with the aerosol concentration ties the increased toxicity quite definitely to the particulate matter. This fact may be of considerable importance to air pollution toxicology.

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VOL.
1
958/9

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THE ASCENT OF TURBULENT FORCED PLUMES IN A CALM ATMOSPHERE

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(*Received* 23 *August* 1958)

Abstract—This paper gives predictions of the heights of forced plumes generated when smoke or other effluent is discharged vertically into a stably stratified atmosphere under calm conditions. The theory, which is given in outline, is based on an earlier model treatment of plumes and assumes that mean profiles across the plume of vertical velocity and excess potential temperature are of similar form at all heights and have widths in constant ratio, and that the inflow velocity due to mixture at the plume edge is proportional to the mean vertical velocity within the plume. There are two undetermined constants in the theory, and values for these are deduced from published data on jets and plumes.

The forced plume from an actual source discharging a stream of buoyant effluent can always be related to a virtual point source of heat and momentum only, and the treatment shows how the position of the virtual source may be found. The ascent of forced plumes in a stable atmosphere with a linear profile of potential temperature is then investigated in terms of these virtual sources; it is shown that the height of the plume-top at first decreases as the momentum flow from the virtual source is increased from zero, and then increases without limit. The discharge of cold effluent is also considered.

The practice of discharging stack gases at high velocity does not provide a practical method of increasing plume heights in calm weather, for the mechanical energy needed to give even a moderate increase in the plume height is quite prohibitive.

VOL
1
1958/

1. INTRODUCTION

WHEN a steady stream of hot gas is discharged vertically into the atmosphere from a chimney a buoyant plume will rise above the chimney-top. The flow in atmospheric plumes on this scale may be assumed turbulent; for if the issuing stream is laminar, it will rapidly become unsteady and then turbulent (YIH, 1951, on the stability of laminar thermal plumes). The ascent of turbulent buoyant plumes from steady sources of heat in a stably stratified atmosphere has been treated by PRIESTLEY and BALL (1955) who were concerned specially with plumes rising from heated surfaces, and by MORTON *et al.* (1956) who investigated the plumes due to steady streams of buoyant fluid issuing from nozzles (but did not take account of the flux of mass or momentum from the source).

The main purpose of this paper will be to find the height to which thermal plumes will rise in a calm stably stratified atmosphere when they are generated from sources which release a stream of hot gas (with appreciable mass and momentum flow). The results can be applied directly to the discharge of smoke and other effluent from chimneys. Such sources will be specified by giving the steady rates of flow of heat, mass of gas, and gas momentum from the chimney-top. The corresponding plumes will be called *forced plumes* because of their initial upward momentum; they can be investigated by an extension of the methods used already by MORTON *et al.* There are two limiting cases of the forced plume: the pure *plume* emitted from a source of buoyancy only, and the *jet* from a source of momentum only.

The treatment has been restricted to reasonably calm atmospheric conditions so that local mixing of plume gas and ambient air will depend only on the turbulence within the plume. Thus no attempt has been made to estimate the effect on entrainment of wind turbulence, nor of inclination of the plume. It has been assumed also that local variations in temperature are everywhere small relative to some reference temperature, so that the effect of large density differences on turbulent mixing across the plume edge need not be considered. Large density differences can occur only near the source and are quickly reduced as the fluid rises; hence this assumption will introduce little error except in the neighbourhood of the source, where the solution is worst in any case (there may also be transition to turbulence).

An advantage of associating plumes with jets is that the extensive experimental knowledge of jets can be used to provide a new estimate for the entrainment constant, α, which MORTON *et al.* introduced as the ratio of the mean speed of inflow at the edge of the plume to the mean vertical speed on the plume axis.

2. THE MODEL FOR FORCED PLUMES

In order to formulate the problem so that it may be solved mathematically, it will be necessary to make two main assumptions about the flow in convective plumes: (1) that profiles of mean vertical velocity and excess temperature (or buoyancy) are each of similar form at all heights in the plume, and (2) that the rate of entrainment at the edge of the plume is proportional to the mean vertical velocity on the axis.

It is a matter of observation that profiles in plumes and jets are almost Gaussian except near the source and in regions where the flow is diverted horizontally because of stratification in the ambient fluid; hence the similarity assumption should be satisfactory throughout most of a forced plume. Little error will be introduced near the plume-top since relative velocities are small and the entrainment there will be slight, but the solution will be less satisfactory in the neighbourhood of the source where the similarity assumption is unreliable and special features of particular flows have to be ignored (e.g. transition to turbulence, peculiarities of the source, effects due to accelerating streams, etc). Once the similarity hypothesis has been accepted it follows that any form of profile can be used in the calculation without loss of genuine physical information. Here it will be simplest to work with " top-hat " profiles, for which a variable is zero outside the plume and constant across the plume section.

Although MORTON *et al.* (1956, hereafter called paper I) took the same width for their velocity and buoyancy profiles, there is actually greater sideways spread of heat than of vertical momentum. For example, ROUSE *et al.* (1952) have made measurements in plumes above gas flames, and have combined a wide range of experimental results in the velocity profile $\exp(-96r^2/z^2)$ and the excess temperature profile $\exp(-71r^2/z^2)$ where r is the radial distance from the plume axis and z the height above a suitable origin. If this difference in widths is ignored and the plume model based on the velocity profile, the predicted buoyancy forces are too large and the penetration of the plume is overestimated. This variation in spread can be allowed for by taking a velocity profile with radius $R = R(z)$ and an associated buoyancy profile (of the same " top-hat " shape) with radius λR.

It has been assumed implicitly that there is turbulence of similar character in all forced plumes. This is likely to provide an adequate working hypothesis except in

VOL.
1
58/9

the neighbourhood of the source, since measured velocity profiles are all approximately Gaussian and there should be approximate local equilibrium of the turbulence. Hence the entrainment constant should be roughly the same for all forced plumes, since it depends only on the turbulent motion within the plume. The value to be used for the entrainment constant depends on the profile shape. (As the " mean edge " of a plume is not clearly defined α is necessarily an artificial quantity, but it represents the inflow from the plume axis.)

The investigation of forced plumes from sources of finite size in stably stratified environments is simplified by the introduction of equivalent point (or virtual) sources. A finite source discharging buoyancy, mass and momentum can always be replaced by a point source of buoyancy and momentum only* (see MORTON, 1959, hereafter called paper II). Moreover, variations in buoyancy with height are due partly to mixing and partly to stratification of the surroundings; in the lower parts of a forced plume the effect of mixing is dominant to such an extent that the ambient fluid may be taken as uniform in finding the position of a virtual source. This is shown by a comparison of the widths of pure plumes from point sources of buoyancy in uniform and in stably stratified environments (see paper I); stratification leads to <1 per cent increase in width at one-third of the plume height, 3 per cent at half the height and <8 per cent at two-thirds of the height to the plume-top. Similarly for vertical jets from point sources of momentum (see paper II) stable stratification causes <2 per cent increase in width half way up the jet, and 5 per cent increase at two-thirds of the jet height.

3. THE EQUATIONS FOR FORCED PLUMES IN A STRATIFIED ATMOSPHERE

The behaviour of axially symmetrical forced plumes generated from horizontal circular sources will be investigated by means of equations which represent the conservation of (i) volume, (ii) momentum and (iii) heat. The treatment (as in papers I and II) was developed for fluids which are incompressible but suffer changes in density on heating; for convection in the atmosphere the theory is analogous provided that potential temperatures and densities are used exclusively. Suppose that $w = w(z)$ is the mean vertical velocity in the plume, $R = R(z)$ the mean radius of the " top-hat " profile, and $\rho = \rho(z)$ the potential density within the plume and ρ_a the potential density of the ambient air; and let the suffix 0 refer to conditions at the source.

The equations for the conservation of volume (or of mass), momentum and heat can be written

$$\left.\begin{aligned} &\frac{d}{dz}(\pi R^2 w) = 2\pi R\alpha w, && \text{(i)}\\ &\frac{d}{dz}(\pi R^2 w^2 \rho) = \pi\lambda^2 R^2 g(\rho_a - \rho), && \text{(ii)}\\ &\frac{d}{dz}[\pi R^2 w(\rho_{a0} - \rho)] = 2\pi R\alpha w(\rho_{a0} - \rho_a), && \text{(iii)} \end{aligned}\right\} \quad (1)$$

* There can be no mass flow from a point source when the momentum flow is finite; for the momentum flow is of order (plume radius)^2 $\times$ (plume velocity)^2 so that the plume velocity near such a point is of order (plume radius)$^{-1}$, and the mass flow is of order (plume radius)^2 $\times$ (plume velocity) which tends to zero at the source.

where αw is the velocity of inflow at the plume edge, $r = R$, and where the heat is measured in terms of the potential density relative to air at source level. Certain correlation terms are omitted from equations (1) in order to obtain a workable set; their omission will be compensated to some extent because α and λ are found experimentally from measurements on jets and plumes. With the use of (1 i), equation (1 iii) can be written in the alternative form

$$\frac{d}{dz}[\pi R^2 w(\rho_a - \rho)] = \pi R^2 w \frac{d\rho_a}{dz}. \tag{2}$$

Since the variations considered in the potential density are small with respect to ρ_{a0}, the value ρ occurring in the left-hand side of equation (1 ii) can be replaced by ρ_{a0} without appreciable error, and the conservation equations can then be written,

$$\left.\begin{aligned} &\frac{d}{dz}(R^2 w) = 2\alpha R w, && \text{(i)}\\ &\frac{d}{dz}(R^4 w^4) = 2\lambda^2 (R^2 w)\left(R^2 w g \frac{\rho_a - \rho}{\rho_{a0}}\right), && \text{(ii)}\\ &\frac{d}{dz}\left(R^2 w g \frac{\rho_a - \rho}{\rho_{a0}}\right) = R^2 w \frac{g}{\rho_{a0}} \frac{d\rho_a}{dz}. && \text{(iii)} \end{aligned}\right\} \tag{3}$$

It should be borne in mind that $R^2 w$ is proportional to the volume flow (and hence approximately to the corrected mass flow), $R^2 w^2$ is proportional to the momentum flow, and $R^2 w g(\rho_a - \rho)/\rho_{a0}$ is proportional to the buoyancy flow (and hence to the heat flow) across a horizontal section of the plume at height z above the source.

The physical quantities which (together with the stratification) determine the behaviour of convection in the greater part of the plume are the rates of discharge of heat (in terms of buoyancy $[\pi\lambda^2 |R^2 w| g(\rho_a - \rho)]_{z=0}$), volume ($[\pi |R^2 w|]_{z=0}$), and momentum ($[\pi |R^2 w| w\rho]_{z=0}$). Although these rates are the actual rates of discharge from the source, the quantities R, w and $g(\rho_a - \rho)$ must be related to the source radius and the discharge velocity and buoyancy in a way which will depend on the choice of plume profiles, and with two " top-hat " profiles the boundary conditions at the source ($z = 0$) are: $R = R_0$ = radius of the source orifice, $w = w_0$ = mean velocity of flow (averaged over the area of the source and time) from the source orifice and $\lambda^2 g(\rho_a - \rho) = \lambda^2 g(\rho_a - \rho)_{z=0}$ = mean buoyancy force (space and time average) over the source orifice.

Heights of forced plumes in a stably stratified atmosphere

In this section a solution is outlined for equations (3) which will permit the prediction of the height, H, of the plume-top above a virtual source in a stably stratified atmosphere (this solution is developed in detail in paper II).

The forced plumes considered here are discharged upwards with effluent gas which may be either lighter or heavier than the ambient air. At the corresponding point sources the momentum flow must be such as to produce the appropriate mass flow at the actual source; when this mass flow is small the momentum flow from the point source will be directed upwards, and when it exceeds a certain value the momentum flow from the point source will be directed downwards (so that there is greater production of mass flow of the entrained air in the fictitious part of the

VOL. 1 58/9

equivalent plume). Thus it will be necessary to deal with point sources which discharge positive or negative buoyancy with positive or negative (measured upwards) momentum. *Only the case of a uniformly stratified atmosphere will be considered.*

The character of solutions to equations (3) must depend on the physical quantities specified in the problem, that is on the rates of discharge of buoyancy and momentum from the virtual source and on the stratification of the atmosphere, and these can be represented by

$$|R_0^2 w_0| \, g \frac{\rho_{a0} - \rho_0}{\rho_{a0}}, \quad |R_0^2 w_0| \, w_0 \quad \text{and} \quad -\frac{g}{\rho_{a0}} \frac{d\rho_a}{dz},$$

respectively. Just one non-dimensional parameter can be formed from these three quantities, and this can be taken in the form

$$-\frac{g}{\rho_{a0}} \frac{d\rho_a}{dz} (|R_0^2 w_0| \, w_0)^2 \left(|R_0^2 w_0| \, g \frac{\rho_{a0} - \rho_0}{\rho_{a0}} \right)^{-2},$$

or as

$$\frac{w_0^2 g \rho_{a0} (d\rho_a/dz)}{w_0^2 g \rho_{a0} (d\rho_a/dz) - \lambda^3 g^2 (\rho_{a0} - \rho_0)^2} = \tau, \text{ say ;} \tag{4}$$

this non-dimensional constant τ will be representative of the behaviour of the plume, and hence the heights of plume-tops above a variety of sources in stratified atmospheres will depend only on τ; that is $H = H(\tau)$. If the plume profiles at different heights are not similar there will be a second dimensionless parameter which will include the height z.

The height H is the distance above the virtual source to the level at which the mean vertical velocity of the plume gas is zero. There are two steps involved in finding H from equations (3). First, equations (3 ii) and (3 iii) are combined by eliminating $R^2 w$ between the right-hand sides, and integrating; this gives a relation between the momentum flux and the buoyancy flux at each level of the plume. Second, z is eliminated between equations (3 i) and (3 ii), and the buoyancy flux is substituted from the first integral; the resulting differential equation can be integrated numerically (with the use of tables of incomplete beta functions for ranges in which these are tabulated). The solution is of the form

$$H = 2^{-\frac{1}{3}} \alpha^{-\frac{1}{3}} \lambda^{-\frac{2}{3}} \left| R_0^2 w_0 g \frac{\rho_{a0} - \rho_0}{\rho_{a0}} \right|^{\frac{1}{3}} \left(-\frac{g}{\rho_{a0}} \frac{d\rho_a}{dz} \right)^{-\frac{1}{3}} H_1(\tau), \tag{5}$$

where

$$\left| R_0^2 w_0 g \frac{\rho_{a0} - \rho_0}{\rho_{a0}} \right|^{\frac{1}{3}} \left(-\frac{g}{\rho_{a0}} \frac{d\rho_a}{dz} \right)^{-\frac{1}{3}}$$

is the scale length formed from the given physical parameters, and the form of the dimensionless height $H_1(\tau)$ depends on the source conditions (see paper II).

Fig. 1 shows a set of curves of the non-dimensional height $H_1(\tau)$ of the plume-top plotted against the parameter τ for the following combinations of momentum and buoyancy flux (which cover all point sources and hence all finite sources from which effluent is discharged upwards—see Section 4):

(1) Curve 1 is for a point source delivering positive buoyancy and positive momentum. The limiting case $\tau = 0$ corresponds with the simple plume from a

VOL 1 1958/

virtual source of buoyancy only, and the greatest non-dimensional height reached by the plume fluid is then $H_1(0)=2{\cdot}805$; a complete solution for the case $\tau=0$ is presented in paper I. As τ is increased, the non-dimensional height decreases, at first rapidly owing to the sudden increase in mixing near the source, and then more slowly. When $\tau>0{\cdot}8$ the effect of momentum flux begins to dominate that of buoyancy, and forced plumes can be projected to any height by sufficiently increasing the momentum as the effluent leaves the source. But this is a very wasteful method of projecting effluent to great heights; for example, it may be noted that

$$\frac{\rho_{a0}w_0^2}{g(\rho_{a0}-\rho_0)^2}\left(-\frac{d\rho_a}{dz}\right)$$

must be increased (from zero) to about 100 *before the height of the forced plume is again as great as that of the simple plume from a virtual source of buoyancy only.* (The actual heights are directly proportional to dimensionless heights if only the momentum flux is varied.)

(2) Curve 2 is for a point source delivering negative buoyancy and positive momentum. A relatively small flux of momentum is needed to lift the plume-top well

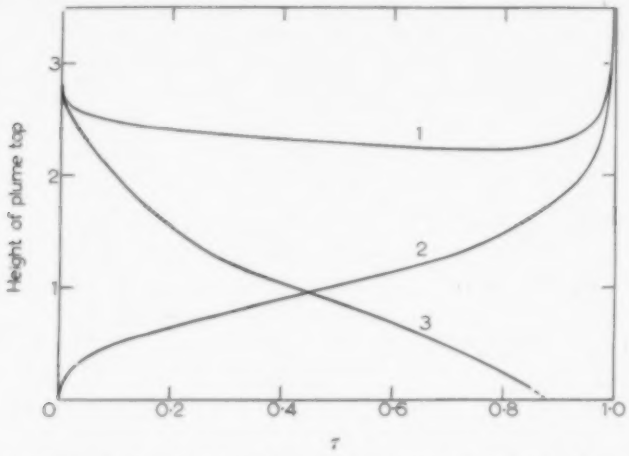

FIG. 1. The non-dimensional height $H_1(\tau)$ of the top of a forced plume above its virtual source in a stably stratified environment plotted as a function of the dimensionless parameter

$$\tau=\frac{w_0^2g\rho_{a0}\,(d\rho_a/dz)}{w_0^2g\rho_{a0}\,(d\rho_a/dz)-\lambda^2g^2(\rho_{a0}-\rho_0)^2}$$

(which provides a measure of the relative importance of stratification and of the flux of buoyancy and momentum from the virtual source). Curve 1 is for a point source which delivers heat and upward momentum, curve 2 for one delivery cold and upward momentum, and curve 3 for heat and downward momentum. These cases include virtual sources for all finite sources discharging either hot or cold effluent upwards.

clear of the virtual source, but thereafter the height increases slowly with increasing momentum. The parts of curves 1 and 2 near $\tau=1$ are very similar, because in this region the flux of momentum from the source completely dominates the forced plume.

(3) Curve 3 is for a point source delivering positive buoyancy and negative momentum. The flow in this case is at first downwards until the plume reaches its

VOL.
1
58/9

lowest level (this belongs to the fictitious part of the flow) and then upwards to the level of the plume-top (shown relative to the virtual source in the figure). Again the effect of additional momentum from the virtual source is to reduce the non-dimensional height of the plume-top for a given flux of buoyancy.

4. POSITION OF THE VIRTUAL POINT SOURCE

The results of Section 3 cannot be applied to the plumes from finite sources until the positions of the corresponding point sources have been determined (and, indeed, it has been shown that these virtual sources do exist). Variations in density of the ambient air have so little effect on the behaviour of the lower half of a forced plume that it will be sufficient for this purpose to ignore stratification and to treat the atmosphere as though at uniform potential temperature or density. This approximation will introduce appreciable error only when the depth, say h, of the virtual source below the actual source proves to be of the same order as the plume height, H; the applications considered in a later section show that $h \ll H$ for atmospheric forced plumes. The neglect of stratification here will simplify the calculations a good deal.

In a uniform atmosphere the flux of buoyancy remains constant at all heights and hence the local buoyancy force is inversely proportional to the local volume flow; the remaining conservation equations reduce to

$$\left.\begin{aligned} &\frac{d}{dz}(R^2w) = 2\alpha Rw, && \text{(i)}\\ &\frac{d}{dz}(R^4w^4) = 2\lambda^2 R^2 w R_0^2 w_0 g \frac{\rho_a - \rho_0}{\rho_a}. && \text{(ii)} \end{aligned}\right\} \quad (6)$$

R_0 is here the radius of the finite source, w_0 the mean velocity (space and time average) over the source and $\lambda^2 g(\rho_a - \rho_0)$ the mean buoyancy there. The character of forced plumes in a uniform environment can depend only on the buoyancy flux, the momentum flux and the volume flux from the source, that is on $R_0^2 w_0 g(\rho_a - \rho_0)/\rho_a$, $R_0^2 w_0^2$, and $R_0^2 w_0$. The only dimensionless group which can be formed from these is

$$\left(R_0^2 w_0 g \frac{\rho_a - \rho_0}{\rho_a}\right)(R_0^2 w_0)^2 (R_0^2 w_0^2)^{-\frac{5}{2}} \equiv g(\rho_a - \rho_0) R_0 / \rho_a w_0^2,$$

which may be written in the alternative form

$$1 - \frac{5\lambda^2 g(\rho_a - \rho_0) R_0}{8\alpha \rho_a w_0^2} = \gamma^5, \text{ say}; \quad (7)$$

in this case the depth of the virtual source below the actual source will be $h = h(\gamma)$.

One integral is obtained from equations (6) after eliminating z, and a second integral after differentiating (6 ii) with respect to z and eliminating $d(R^2w)/dz$, and these integrals provide a parametric solution in terms of Rw. In paper II this parametric solution is used in a full investigation of the behaviour of forced plumes in a uniform atmosphere, and the relationship between plumes, forced plumes and jets is demonstrated. It is also shown that for every finite source $\{R_0^2 w_0 g(\rho_a - \rho_0)/\rho_a, R_0^2 w_0^2, R_0^2 w_0\}$ there exists a virtual point source $\{R_0^2 w_0 g(\rho_a - \rho_0)/\rho_a, \gamma^2 R_0^2 w_0^2, 0\}$ at a depth $h = (R_0^2 w_0^2)^{\frac{1}{2}} \mid R_0^2 w_0 g(\rho_a - \rho_0)/\rho_a \mid^{-\frac{1}{2}} h_1(\gamma)$ below the given source, such that both sources produce identical plumes above the level of the actual source.

$(R_0^2 w_0^2)^{\frac{1}{2}} / |R_0^2 w_0 g(\rho_a - \rho_0)/\rho_a|^{-\frac{1}{3}}$ is the appropriate scale length and $\frac{1}{2}h_1(\gamma)$ a non-dimensional depth. The following cases may be distinguished :

(*a*) When $0<\gamma<1$, the forced plumes behave as though from a virtual source of positive buoyancy and positive momentum at a distance below the finite source

$$h_1 = 2^{-\frac{1}{3}}5^{\frac{1}{3}}\alpha^{-\frac{1}{3}}\lambda^{-\frac{1}{3}}\gamma^{\frac{1}{3}}\int_1^{1/\gamma}(t^5-1)^{-\frac{1}{3}}t^3\,dt$$

$$= 4{\cdot}29\gamma^{\frac{1}{3}}\int_1^{1/\gamma}(t^5-1)^{-\frac{1}{3}}t^3\,dt, \qquad (8\text{ i})$$

where the values $\alpha = 0{\cdot}116$ and $\lambda = 1{\cdot}08$ have been substituted.

(*b*) When $\gamma = 0$, there is a virtual source of pure buoyancy at $h_1 = 2{\cdot}86$.

(*c*) When $\gamma<0$, there is a virtual source of positive buoyancy and negative momentum at

$$h_1 = -4{\cdot}29\,|\gamma|^{\frac{1}{3}}\int_{-1}^{1/|\gamma|}(t^5+1)^{-\frac{1}{3}}t^3\,dt, \qquad (8\text{ ii})$$

below the source; but the integral can be positive, in which case the virtual source lies above the actual source. This corresponds to a plume with large volume flow

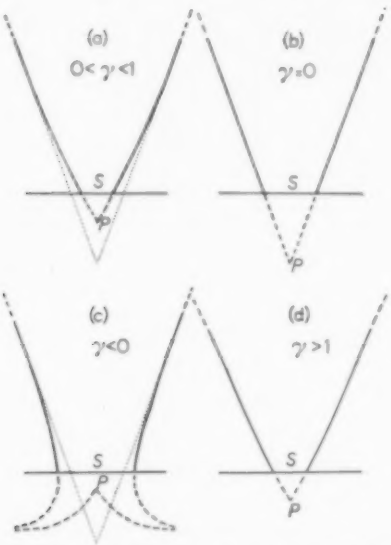

FIG. 2. These sketches show typical positions of the virtual source (*P*) relative to the actual source (*S*), and the appearance of the lower parts of the corresponding forced plumes. The " edge " of the forced plume is shown by continuous lines, and that of the fictitious region by broken lines ; the dotted lines show the simple plume (from a source of heat only) which has the same behaviour as the forced plume far from the source. Case *a* is for a finite source delivering a small flow of hot fluid with large momentum, case *b* delivers a flow appropriate to a simple plume, case *c* delivers a large flow of hot fluid with small momentum, and case *d* delivers cold fluid but is otherwise similar to case *a*.

and small momentum flow from the source; in the lower regions the gas is accelerated by the buoyancy forces.

VOL. 1 58/9

(*d*) When $\gamma > 1$, there is a virtual source of negative buoyancy with positive momentum at

$$h_1 = 4{\cdot}29\gamma^{\frac{1}{3}} \int_{1/\gamma}^{1} (1 - t^5)^{-\frac{1}{2}} t^3 \, dt \,. \tag{8 iii}$$

These different cases may be clearer if the corresponding flow patterns are described. In case (*b*) the flow is straight-sided because the volume flux from the actual source is appropriate to that level in a simple plume; this is sketched in (*b*) of Fig. 2, where the continuous lines represent the edge of the actual forced plume, the broken lines the edge of the fictitious region of the plume, *S* is the actual source and *P* the virtual point source. Dotted lines are drawn where appropriate to show the asymptotic (i.e. simple plume) behaviour, and the departure from this shape near the source. In case (*a*) there is less volume flow (for given buoyancy and momentum flux); *P* is closer to *S* and there is less entrainment between. Close above *S* the forced plume is spreading more rapidly than a simple plume (in fact, more nearly as a jet). In case (*c*) there is increased volume flow at the actual source, and this is produced by a virtual source of negative momentum (which may be below or above *S*). The *fictitious* flow is at first downwards until it spreads sideways at its lowest depth, returns upon itself, and passes through the source *S* with the appropriate rates of flow of buoyancy, momentum and mass. Case (*d*) corresponds with the upward projection of heavy effluent.

5. VALUES FOR THE CONSTANTS λ AND α

The values which will be used in the examples given below *in conjunction with "top-hat" profiles* are $\alpha = 0{\cdot}116$ for the entrainment constant and $\lambda = 1{\cdot}08$ for the spreading ratio.

This value for λ has been obtained for thermal diffusion from the profiles recommended by ROUSE *et al.* (1952).

The experimental determination of α described in paper I (in which a plume of alcohol was released in a tank of stably stratified salt solution) cannot be regarded as wholly satisfactory, as the following comments indicate: the entry length (KUETHE, 1935) was as much as one-quarter of the plume height in some runs; the release of alcohol was so short that time-dependent effects would have been included; when alcohol mixes with water there is a reduction in volume up to 5–10 per cent; the tank diameter was only 10 times that of the main nozzle. These objections would not apply to steady jets of air in the atmosphere, and so a value of α more nearly representative of the basic turbulent mixing processes should be found from results for jets, provided that measurements are taken far enough from the nozzle.

The equations for a jet in a uniform environment can be reduced from equations (3) to the form

$$\frac{d}{dz}(R^2 w) = 2\alpha R w, \quad \frac{d}{dz}(R^4 w^4) = 0, \tag{9}$$

with the solutions

$$R = R_0 + 2\alpha z = 2\alpha\left(z + \frac{R_0}{2\alpha}\right),$$

$$w = \frac{R_0 w_0}{R_0 + 2\alpha z} = \frac{R_0 w_0}{2\alpha(z + R_0/2\alpha)}.$$

Hence the jet may be regarded as coming from a virtual point source at $z = -R_0/2\alpha$.

These results can now be compared with the known experimental behaviour of jets to give a new value for α, and this comparison must be made with quantities integrated across the plume because of the choice of profiles. According to the simple treatment above, the mass flux at distance z from the virtual source of a jet is

$$\pi\rho R^2 w = 2\pi\alpha\rho R_0 w_0 z.$$

This may be compared with the value $0{\cdot}404\pi^{\frac{1}{2}}\rho R_0 w_0 z$, which is given by SCHLICHTING (1955, Chapter 23) from experiments carried out by REICHARDT (1942), and the corresponding value for α is 0·115. Similar comparisons have been made with experimental results given by SQUIRE (1950), KUETHE (1935) and RUDEN (1933), and the corresponding values for the entrainment constant are 0·119, 0·112, and 0·117. Although these determinations vary in reliability, it is clear that the value of the entrainment constant based on jets and for the " top-hat " profile is reasonably close to 0·116. There is evidence that the value of α may increase a little from the jet to the plume, but it is hard to determine this variation very precisely from the published experimental data. In any case, the effect on plume height will not be large because only the square root of α is involved, and hence the value 0·116 will be used here. This question will be discussed elsewhere. (The corresponding values of the entrainment constant for Gaussian profiles are obtained on dividing by $\sqrt{2}$.)

6. APPLICATIONS TO ATMOSPHERIC CONVECTION

The design of a chimney to disperse spent furnace gases from an industrial or electrical power plant involves a definite choice of source conditions for the smoke plume. In many cases the power requirements are roughly constant, and hence the loss of heat to the atmosphere $[\propto R_0^2 w_0 g(\rho_{a0} - \rho_0)/\rho_{a0}]$ will be steady and can be calculated from the known efficiency of the plant. There is a minimum value of air flow for complete combustion of the fuel, but in practice $R_0^2 w_0$ is likely to be rather larger because of incomplete burning of the oxygen in the air stream or the addition of other gases between the furnace and the chimney. When $R_0^2 w_0$ is known, the velocity at which smoke issues depends on the diameter of the chimney-top. The height of the plume-top is then the value which has been predicted for this source plus the height of the chimney. Suppose that a particular furnace gives up heat to the exhaust gases at the rate of 1×10^5 kW, and that these gases are then to be discharged from a suitable chimney into (*a*) an I.C.A.N. standard atmosphere (i.e. ground temperature 288°K, decrease of temperature with height 6·5°C/km), or (*b*) an inversion with ground temperature 288°K and increase of temperature 2°C/km. If this heat were released from a virtual source of pure buoyancy the resulting plumes would rise to heights (*a*) 862 and (*b*) 535 m, respectively; Table 1 shows the corresponding heights $H - h$, given in metres, to which the plume rises above its actual source (i.e. the chimney-top) for a wide range of initial conditions (R_0 and w_0) which includes typical cases (BRYANT and COWDRAY, 1955; BEST, 1957). The information given for each pair of values of the volume flux ($\pi R_0^2 w_0$ m³/sec) and exit velocity (w_0 m/sec) is as follows: (i) the parameter γ^5, which relates the exit values of the buoyancy, momentum and volume flow rates and from which the position of a virtual source can be found, (ii) the depth h (m) of the virtual source below the chimney-top, (iii) the parameter τ, which is characteristic of the relative effects of momentum

VOL.
1
58/9

and buoyancy effects from a source in a stratified atmosphere, and the height $H-h$ (m) of the plume-top above the chimney-top for the I.C.A.N. standard atmosphere, and (iv) τ and $H-h$ for the inversion of 2°C/km. The number of significant figures given is intended to bring out small differences between the results and is not an indication of confidence in the absolute heights estimated. These results show that, under

TABLE 1

w_0 (m/sec)		$\pi R_0^2 w_0$ (m³/sec)			
		250	500	750	1000
	γ^5	−10·20	−6·92	−5·47	4·60
	h	11	16	19	22
5	τ	0·00010	0·00035	0·00070	0·00110
	$H-h$	841	830	820	814
	τ	0·00036	0·00125	0·00250	0·00393
	$H-h$	516	507	500	494
	γ^5	0·281	0·492	0·585	0·641
	h	12	16	19	21
15	τ	0·00005	0·00040	0·00105	0·00200
	$H-h$	845	834	825	818
	τ	0·00018	0·00143	0·00375	0·00715
	$H-h$	517	506	497	490
	γ^5	0·800	0·858	0·884	0·900
	h	6	7	7	8
25	τ	0·00040	0·00175	0·00400	0·00720
	$H-h$	844	833	824	816
	τ	0·00143	0·00626	0·01430	0·02575
	$H-h$	516	505	497	488

The behaviour of smoke plumes from a source of strength 1×10^5 kW in a stably stratified calm atmosphere for different values of volume flux ($\pi R_0^2 w_0$ m³/sec) and exit velocity (w_0 m/sec) from the chimney. The parameters γ^5 and τ are characteristic of the plume, h is the depth in metres of the virtual source below the chimney-top, and $H-h$, the height in metres of the plume top above the chimney. The first pair of values (τ, $H-h$) is in each case for a source in an I.C.A.N. standard atmosphere, and the second pair for an inversion in which the temperature rises by 2°C/km.

normal working conditions for a furnace of this kind, *the effect of discharging momentum from this source of buoyancy in a stably stratified environment is always to reduce the height of the plume*. However, for the range of output conditions considered, the greatest reduction in height is only about 5 per cent and the effect of buoyancy is clearly dominant in all the plumes—alternatively, this dominance is shown by the small values of τ. In each case the virtual source is close to the actual source, so that errors introduced by the approximate determination of h are likely to be small. It would, of course, be possible to give a complete treatment for the

forced plume from the source (R_0, w_0, $g\overline{\rho_{a0}-\rho_0}$) in a stratified environment, but the labour involved would not be justified by the additional return of information. One inference from the results in Table 1 is that for calm weather conditions *the discharge of smoke by pumping at increased speeds from short chimneys cannot be as effective in dispersing the smoke as normal discharge from taller chimneys.*

TABLE 2

$\pi R_0^2 w_0 g \frac{\rho_{a0}-\rho_0}{\rho_{a0}}$ (kW)	$\pi R_0^2 w_0$ (m³/sec)			
	250	500	750	1000
1×10^5	845	834	825	818
$0{\cdot}67 \times 10^5$	757	744	734	725
$0{\cdot}33 \times 10^5$	628	613	600	588
0	153	180	197	210

The height ($H-h$ m) from chimney-top to plume-top for a range of volume flux ($\pi R_0^2 w_0$ m³/sec) and heat flux ($\pi R_0^2 w_0 g[\rho_{a0}-\rho_0]/\rho_{a0}$ kW) from the chimney. In each case the exit velocity is 15 m/sec and the plume rises in an otherwise calm I.C.A.N. standard atmosphere.

In some plants the furnace gases are washed to remove sulphur dioxide before discharge into the atmosphere. This has two effects: (i) the heat flux from the chimney is reduced, and (ii) the saturated stream carries water droplets which evaporate as ambient air is entrained causing further loss in buoyancy. The latter effect can be taken into account quantitatively by including a conservation equation for water, but it is interesting to show how large an effect can be produced by the initial cooling alone. An illustration of this is given in Table 2, which shows the heights $H-h$ (m) from chimney-top to plume-top in an I.C.A.N. standard atmosphere for the previous range of volume discharge ($R_0^2 w_0$) with the single exit velocity $w_0 = 15$ m/sec, and with 1, 2/3, 1/3 and 0 times the heat output of the previous example (1×10^5 kW). These results bring out the fact that *small reductions in the strength of the heat source have relatively little effect on the height of the plume*, but that *substantial reductions in the supply of heat have a very large effect indeed.* Moreover, *the effect of large losses in buoyancy cannot in practice be offset by increasing the momentum flux*—for example, an exit velocity of 3000 m/sec would be needed to lift the top of the " cold " plume

$$\left(\pi R_0^2 w_0 g \frac{\rho_{a0}-\rho_0}{\rho_{a0}} = 0, \quad \pi R_0^2 w_0 = 1000 \text{ m}^3/\text{sec}, \quad -\frac{g}{\rho_{a0}}\frac{d\rho_a}{dz} = 1{\cdot}13 \times 10^{-4}\right.$$

for the I.C.A.N. standard atmosphere) to the original height of 862 m!

Stable stratification of the atmosphere has a very obvious effect on the plumes of smoke from household chimneys. Table 3 shows values for the parameter τ and the height $H-h$ (m) of the plume-top above the chimney-top for the smoke from a fire burning about 1 kg coal per hour (taken as a 5 kW source) and discharging through a chimney pot of area 200 cm². The rates of air-flow ($\pi R_0^2 w_0$ l/sec in this case) vary from the minimum necessary for combustion to a strong draught, and the values taken for $-\frac{g}{\rho_{a0}}\frac{d\rho_a}{dz}$ correspond with temperature decreases of 8·5°C/km, 6·5°C/km

(I.C.A.N. standard), 0°C/km, and a rise of 5°C in 40 m (for a strong inversion on a clear autumn evening). It may be observed that *relatively little reduction is caused in the height of the plume when the air-flow through the fire is not regulated.*

TABLE 3

$-\frac{g}{\rho_{a0}}\frac{d\rho_a}{dz}\times 10^6$		$\pi R_0^2 w_0$ (l/sec)			
		5	20	80	200
0·044	τ	$2{\cdot}31\times10^{-7}$	$1{\cdot}63\times10^{-6}$	$1{\cdot}91\times10^{-4}$	$7{\cdot}74\times10^{-3}$
	$H-h$	103	103	102	98
0·113	τ	$5{\cdot}94\times10^{-7}$	$4{\cdot}18\times10^{-6}$	$4{\cdot}91\times10^{-4}$	$1{\cdot}96\times10^{-2}$
	$H-h$	72	72	71	68
0·334	τ	$1{\cdot}76\times10^{-6}$	$1{\cdot}24\times10^{-5}$	$1{\cdot}45\times10^{-3}$	$5{\cdot}59\times10^{-2}$
	$H-h$	48	48	47	40
4·60	τ	$2{\cdot}42\times10^{-5}$	$1{\cdot}70\times10^{-4}$	$1{\cdot}96\times10^{-2}$	$4{\cdot}49\times10^{-1}$
	$H-h$	18	18	17	15

The behaviour of the plumes of smoke from a household fire for different rates of air-flow ($\pi R_0^2 w_0$ l/sec) and a range of stable stratifications in the atmosphere $[-(g/\rho_{a0})(d\rho_a/dz)]$. $H-h$ is the height in metres to which the smoke rises above the chimney; the fire is burning about 1 kg coal/hour and the area of the chimney-pot is 200 cm².

In each of the previous examples heat is released at a constant rate into some air stream. A completely different kind of example is provided by the exhalation of cigarette smoke, in which case the breath temperature may be taken as constant and

TABLE 4

Mouth aperture (cm²)		$\pi R_0^2 w_0$ (cm³/sec)			
		150	250	500	750
5	γ^5	0·726	0·901	0·975	0·989
	h	0·06	0·06	0·06	0·06
	τ	0·0046	0·0150	0·0607	0·1286
	$H-h$	1·82	2·01	2·30	2·47
1	γ^5	0·9951	0·9982	0·9996	0·9998
	h	0·03	0·03	0·03	0·03
	τ	0·1288	0·2917	0·6224	0·7882
	$H-h$	1·67	1·83	2·08	2·29

The behaviour of plumes of cigarette smoke blown vertically in a room with a stable stratification of ¼°C/m. The results, which are shown for four rates of breathing ($\pi R_0^2 w_0$ cm³/sec) and two mouth apertures, include the parameter γ^5, the depth (h metres) of the virtual source, the parameter τ, and the height ($H-h$ m) to which smoke rises.

the supply of heat to the forced plume depends on the rate of breathing. Suppose that the breath temperature is 34°C, and that the smoker is in a large room in which the air temperature at head level is 18°C and increases with height by ¼°C/m. Table 4

shows the behaviour of the smoke plume for four rates of breathing ($\pi R_0^2 w_0$ cm^3/sec) and two different mouth apertures, 5 cm^2 for an open mouth, and 1 cm^2 for pursed lips.

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VOL.
1
958/9

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THE BEHAVIOUR OF CHIMNEY PLUMES

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Abstract—The formulae available for computing the pollution due to an isolated chimney are too complicated to be of any practical use. The weather conditions in which they are correct are not usually the most important that can occur. Therefore, some simpler formulae are proposed: but these have to be used with discretion and with an understanding of the complexities of the actual weather.

The rise due to efflux momentum and buoyancy is calculated using simple formulae derived by dimensional analysis and simple experimental constants. The plume is assumed to be bent over when the upward velocity is about equal to the wind speed and the rise is assumed to be complete when the upward velocity is reduced to a certain fraction of the wind speed. When the rise is complete, the effluent is carried passively by the ambient turbulence. The formulae acknowledge three different regimes in which the efflux momentum, the buoyancy, and ambient turbulence successively dominate the mixing process.

When a plume contains liquid water an appreciable amount of heat may be lost when it evaporates on mixing with the environment. A diagram is given for computing the effect on the buoyancy. It may be enough to make the plume sink rapidly to the ground.

Finally it is argued that architects should accept the chimney heights necessary for the proper dispersal of pollution as a requirement and design their buildings with the chimney as an integral part instead of as an undesirable appendage.

VOL
1
1958/

1. THE NATURE OF THE PROBLEM

It is desirable to have formulae which will predict the concentration at a point on the ground of pollution emitted from a chimney some distance away, particularly at times when the pollution tends to accumulate. Many formulae have been proposed but it is not our present purpose to discuss them in detail. As mathematical solutions of special problems posed they are in many cases admirable, displaying insight which we shall make use of; but as analyses of the behaviour of actual smoke in the actual atmosphere they are very inadequate because they treat only special cases which are not of special interest. In many the degree of mathematical complication is not justified because the answers they give are only crude approximations to what in fact happens, and it is our purpose to suggest simpler formulae which can be applied with understanding by engineers. The well known $2\frac{1}{2}$ times rule concerning chimney heights is commendable because it is comprehensible as a practical working rule: it has no precise theoretical justification, and if experience proved it to be inadequate it could be changed by Act of Parliament!

As legislation is improved and it is desired to set limits to permissible concentrations of pollution, the weather conditions under which the concentrations are to be calculated will have to be prescribed. This is probably the crux of the problem because under average or typical conditions there is unlikely to be a pollution nuisance. Serious damage by pollution must be guarded against, particularly on those few occasions when there are light winds and stable temperature gradients, and it is to such occasions that *none* of the best known formulae applies.

First we shall see what problems can be solved exactly and consider some of the ways in which actual circumstances render these solutions inapplicable, and raise new problems as yet unsolved. We shall propose some simple formulae.

2. SIMPLE PROBLEMS SOLUBLE BY DIMENSIONAL ANALYSIS AND EXPERIMENT

To begin with we shall consider vertical velocities with which pollution may travel and the concentrations in which it may be found. The simplest cases are those in which such velocities are determined in one single way. Thus in the case of a vertical jet of gas having the same density as the surroundings we can imagine that the vertical velocity of efflux is the only quantity given, or derivable from the data, with the dimensions of velocity, in which case all velocities are necessarily proportional to it. If we then make use of the observation that the pollution is confined to a roughly cone-shaped region we conclude immediately that it must be precisely cone-shaped. For if there is no length other than height above the orifice which can determine the width at that height, since no height is distinguishable specially from another, the width must be a constant multiple of the height.

We cannot involve the velocity in any computation of the width because it involves the dimensions of time, and so all such jets have cones of the same half-angle. This half-angle has to be determined by experiment because the motion is too complicated for any existing analysis to determine it theoretically. It is found to be about 12°.

Clearly the velocity varies as a function of height and so

$$\frac{w}{w_0} = f\left(\frac{z}{z_0}\right)$$

VOL. 1 58/9

where suffix 0 denotes values at one height. The function on the right-hand side can be represented as a power series in $\left(\frac{z}{z_0}\right)$. From the similarity of the jet at all heights we can deduce from the assertion that the flux of upward momentum is the same at all heights that if r is the radius (half-width)

$$w^2 r^2 = \text{const.} = w_0^2 r_0^2.$$

Since $r \propto z$ we must have that

$$w \propto \frac{1}{z} \quad \text{or} \quad \frac{w}{w_0} = \frac{z_0}{z}$$

If σ is the concentration of pollution, since the upward flux of pollution is constant

$$\sigma w r^2 = \text{const.} = \sigma_0 w_0 r_0^2$$

and so

$$\frac{\sigma}{\sigma_0} = \frac{z_0}{z}$$

It is necessary to perform an experiment to determine the distribution of σ and w across the jet. A prediction of these profiles can be made on certain assumptions about the mixing processes but these assumptions are arbitrary in the sense that they are not deduced from the laws of motion of the fluid.

Other cases can be treated in a similar manner. For instance there are a buoyant vertical plume in which the vertical velocity is determined solely by the buoyancy ($g.\Delta\rho/\rho$ denoted in this paper by gB) and distance above the orifice, a solitary mass of air puffed out of an orifice (a puff), and a solitary cloud of buoyant fluid (a " thermal ")

released from rest: these are the simplest cases of motion up a vertical axis. Bent-over plumes of buoyant or non-buoyant effluent can be treated on the assumption that when it has taken up a horizontal speed almost equal to that of the wind, a

TABLE 1

	Vertical jet	Vertical buoyant plume	Vertical puff	Vertical thermal	Bent-over jet (cylindrical puff)	Bent-over buoyant plume (cylindrical thermal)
Vertical velocity w	$w \propto z^{-1}$	$w_{max} = 4{\cdot}7 z^{-\frac{1}{3}} F^{\frac{1}{3}}$ *	$w \propto z^{-3}$	$w \propto z^{-1}$	$w \propto z^{-2}$	$w \propto z^{-\frac{1}{2}}$
Concentration σ or buoyancy gB	$\sigma \propto z^{-1}$	$gB_{max} = 11 z^{-5/3} F^{\frac{1}{3}}$ * $\sigma \propto z^{-5/3}$	$\sigma \propto z^{-3}$	$\sigma \propto z^{-3}$ $B \propto z^{-3}$	$\sigma \propto z^{-2}$	$\sigma \propto z^{-2}$ $B \propto z^{-3}$
Relation between vertical velocity w and buoyancy B	—	$w_{max} = 1{\cdot}4 (gB_{max} z)^{\frac{1}{2}}$ *	—	$w_c = 1{\cdot}2 (g\bar{B}r)^{\frac{1}{2}}$	—	$w_c = 0{\cdot}8 (g\bar{B}r)^{\frac{1}{2}}$
Width r	$z = 4{\cdot}7r$	$z = 5{\cdot}1r$	$z \propto r$	$z = 4r$ †	$z \propto r$	$z = 2{\cdot}25r$
Half-angle of cone α	12°	11°	?	15° †	?	19°
Volume	—	—	?	$3r^3$ †	?	$2{\cdot}5r^2$/unit length
Height as a function of distance downwind	—	—	—	—	$z \propto x^{\frac{1}{2}}$	$z \propto x^{\frac{2}{3}}$

z is measured in all cases from the vertex of the enveloping " cone " at which $r = 0$.

* Values from ROUSE, YIH and HUMPHREYS (1952).

† The shape of thermals is rather variable so that these values can be considered to be measurable to within 25%. The values for the vertical jet and buoyant plume are time average values. It is most convenient to express the properties of the vertical jet and plume in terms of the maximum values of w and B, which, on the average, are found on the axis. For the vertical thermal the mean buoyancy $\bar{B}$ is more significant because it is easily related to the total buoyancy of the thermal : the vertical velocity of the cap w_c is the most convenient velocity to refer to. The vertical puff and the bent-over jet have not been sufficiently studied in the laboratory for some of the numerical values to be given. In the vertical plume and bent-over plume F is the amount of buoyancy emitted in unit time, and is therefore equal to $gB_0 w_0 A$ at an orifice of area A with steady (non-fluctuating) efflux velocity. In the bent-over plume $FU = 2{\cdot}5 g\bar{B}r^2$ for a wind of velocity U. In all cases the effect of ambient turbulence is assumed to be negligible.

vertical section of the plume behaves as if it were a section of a cylindrical puff or thermal. The results, whose derivation has been given elsewhere (e.g. SCORER 1958) are set out in Table 1. It will be seen that the velocity decreases more rapidly when there is no buoyancy to provide new upward momentum.

The height z and horizontal distance x are measured from an origin supposedly

close to the orifice, whose dimensions are assumed to be small compared with the width of the plume so that the distribution of velocity across the orifice is unimportant. Close to the orifice these simple relationships cannot hold.

The distribution of velocity and concentration have been measured in some of the cases in Table 1. For practical purposes the vertical jet and buoyant plume have the same shape of profile which fits a Gaussian curve fairly well except at the edges where the plumes and jets have limits beyond which absolutely no pollution is observed. The bent-over jet and plume do not have circular or elliptical sections such as they are assumed to have in all published theories of them of which I am aware, but look very like the puff and the thermal in having a large, ordered, vertical velocity up the middle, a region of mixing at the upper surface, and a zero or slightly downward velocity at the greatest width. The distribution of motion is shown roughly in Fig. 1. The volume increases as the material rises, both by mixing at the

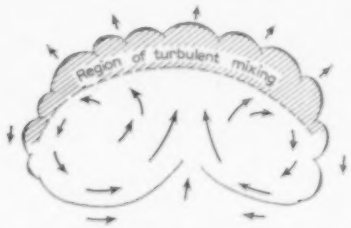

FIG. 1. The distribution of ordered velocity in a thermal or puff. The motion in a section of a buoyant plume or bent-over jet is very similar.

VOL. 1 58/9

upper surface and by ordered entrainment at the rear. The unpolluted material rising up the centre is distributed sideways at the top in an unsteady manner so that if a small volume of pollution were marked it would, after the main body had risen one or two diameters, be found to be well distributed throughout almost the whole volume.

The case of a thermal has been studied extensively by SCORER (1957) and WOODWARD (1958) who have measured the behaviour of the cloud as a whole and the velocity distribution in and around it. A similar exploration of cylindrical thermals will, it is hoped, effectively map the behaviour of bent-over buoyant plumes.

It must be emphasized that all this behaviour occurs only in the absence of any complicating motion of the surroundings. Such motion, aptly described as *ambient turbulence*, may be studied on its own and simple formulae devised on certain assumptions. The most stimulating ideas have come from SUTTON and his associates working primarily on the diffusion of gases from a ground or elevated source over open country in a moderate wind with a neutral temperature gradient (i.e. one in which there are no buoyancy forces affecting the motion).

The most illuminating assumptions are as follows:

(1) That the transfer of material is governed by the same eddy diffusion coefficient as the transfer of momentum. This enables the vertical distribution of horizontal velocity to be used to compute the rate of vertical transfer of material (e.g. SUTTON 1955).

(2) That the turbulent velocities are always the same multiple of the wind velocity.

This would mean that the pollution from an elevated source would always be transferred along the same plume in the same way regardless of the wind speed. Though this assumption may be true in some localities for particular wind directions in a neutral temperature gradient it is not true in general, particularly at low wind speeds when the pollution is important.

(3) That the eddy size which dominates the spreading of the plume is proportional to distance from the orifice and therefore to the width of the plume because the motion is similar at all distances. This means that the plume is conical. This delightful, ingenious, and instructive idea is naive when applied too literally because it ignores many of the complications existing in nature.

(4) That the Richardson number alone determines the way in which the motion in stably or unstably stratified airstreams departs from that of a neutral temperature gradient. Much valuable work has been done, particularly by Priestley and his associates in Australia, in relating the transfer of material and momentum from the ground through the lowest few metres of air to the Richardson number, which is the simplest non-dimensional number relating the static stability forces, represented by $g\beta$ $\left(\beta = \frac{1}{\bar{\theta}} \cdot \frac{\partial \theta}{\partial z}\right.$ in the atmosphere and $\left. -\frac{1}{\bar{\rho}} \cdot \frac{\partial \rho}{\partial z}\right)$ in an incompressible fluid and the inertia forces resulting from shearing motion in the wind, represented by U' $(= \partial U/\partial z$, where U is the wind speed). $Ri = g\beta/U'^2$. The use of a single number of this kind is only justified when the amount of buoyancy and momentum being transferred vertically through the layer under consideration is large compared with the net amount entering it. The layer is then an externally driven machine in which the buoyancy and inertia forces (or Reynolds stresses) enter into a unique relation to one another at a given Richardson number. The technique cannot be applied at times when the layer is being warmed or cooled rapidly or has not a unique Richardson number. Ri can be defined at a point, so that the number $z\partial(\log Ri)/\partial z$ or its profile, may be equally important.

All writers have recognized at some time or another the necessity of taking account of the stability or instability produced by various temperature gradients and some have suggested modified coefficients for use in their formulae in various possible cases. All such attempts have, however, assumed that the temperature gradient is uniform, or follows a simple law with height so that one coefficient alone can describe its effects. The inconvenience of attempting anything more complicated is too great. Yet the temperature gradient in the actual atmosphere is characteristically much greater near the ground than higher up; whether it is stable because the ground is cold or unstable because the ground is hot, it is a serious practical problem to find two heights at which the temperatures should be measured to give a representative temperature gradient. These heights must, strictly, depend on the wind speed, because the temperature profile is greatly affected by the wind.

3. EQUIVALENT STACK HEIGHT

It can be seen from Table 1 that the velocities due to the momentum possessed at efflux or subsequently produced by buoyancy forces decrease ultimately to less than any prescribed magnitude. In particular they will ultimately become negligible in comparison with the velocities of the ambient turbulence. Thereafter the pollution will become passive and will be carried as if it had possessed no buoyancy or efflux

velocity, but had been emitted from a higher source than the actual chimney mouth. The height of the source of non-buoyant material which, when emitted with no vertical velocity, would produce the same pattern of pollution is called the *equivalent stack height*. This is a helpful concept in thinking about the different parts of the plume in which the various influences are dominant (efflux momentum, buoyancy, ambient turbulence; in that order). Its usefulness is restricted by the fact that its value depends upon the magnitude of the ambient turbulence and wind speed, and is not a function of the chimney height and efflux velocity and buoyancy only. Clearly the equivalent height is the actual height in a very strong turbulent wind but is an infinite height if there is no ambient turbulence and the air is not stably stratified. If there is a very stable layer of air (with a rapid increase in temperature upwards) at a small height above the chimney, the plume will reach this height and rise no further if there is no ambient turbulence, in which case the equivalent stack height is determined *only* by the condition of the environment for all ordinary chimneys.

By making certain assumptions about the rate at which a plume is diluted by mixing with the surroundings, BOSANQUET (1957) has derived formulae which give the height to which the effluent will ascend in winds of various speeds with various efflux velocities and buoyancies. His assumptions do not agree precisely with Table 1 because they imply identical laws of dilution in the bent over and vertical parts of the plume. They also imply the same ratio between the mixing velocity (or rate of inflow of environmental air into the plume) and the velocity of the plume relative to the surroundings whether it is due to exit momentum or buoyancy. Table 1 implies that the mixing and relative velocities are proportional in each case, but the constants of proportionality may be different in the various cases. In BOSANQUET's treatment they are deduced not from experiments on similar flows, but by an argument which draws an analogy between the drag on a solid cylinder and the drag due to entrainment on a body of moving fluid.

He assumes also, like many other authors, that the effect of ambient turbulence is determined only by the wind speed. This is an incorrect assumption because it also depends upon the vertical gradients of temperature and velocity, and may vary by several orders of magnitude as these gradients vary. Nevertheless his values are probably fair for an airstream with neither static instability producing thermal convection nor stability suppressing the turbulence, and they predict the possibility of one interesting result which had hitherto only been argued qualitatively (SCORER, 1954) and inevitably disputed. This is that there may be an optimum efflux velocity for a given buoyancy and wind speed. Thus to increase the efflux velocity of a buoyant plume may decrease the equivalent stack height if there is ambient turbulence. The analysis given in the next section confirms this.

When there is thermal convection taking place in the surrounding air a hot plume from a power station or source of similar magnitude may initiate thermals. The average temperature gradient is unstable and the source may therefore determine the location of the up-currents. This is a phenomenon well known to glider pilots who habitually soar in the plumes of cement works, steel works, and power stations. In such cases the plumes rise up to several thousand feet and can often be seen to produce cumulus clouds. The equivalent stack height is then almost infinite, and the pollution is not detected at the ground.

In the evening of a day of thermal convection, the air becomes very stable close

VOL. 1 58/9

to the ground on account of the loss of heat by radiation. This reduces the ambient turbulence for a given wind speed at chimney-top level and the behaviour is often of a type envisaged in Table 1 for bent-over plumes. The plume takes on a more regular outline. The equivalent stack height is still infinite.

In the early morning the turbulence due to the passage of the air over rough ground may be confined to a very shallow layer by the great stability of the air. Because the stable stratification has extended up to above the chimney top, the rise due to buoyancy is small, but a tall chimney may emit its effluent above the layer in which ambient turbulence exists (generally about average building height at this time of day) while a lower one, even though emitting hotter gases may pollute the ground. This property of tall chimneys is not taken into account in any formulae for equivalent stack height or for pollution at the ground, yet it is one of the greatest merits of tall chimneys because it is important especially when the wind is light and pollution is liable to accumulate. It is practicable to build chimneys to a height exploiting this feature of the atmosphere, as can be seen from any vantage point in a large city on an evening free of cloud.

In view of this discussion it is not considered possible to devise a single general formula for equivalent stack height.

4. SOME SIMPLE APPLICATIONS OF TABLE 1

(i) *Calm surroundings; increase of efflux velocity*

(*a*) *Neutrally stratified surroundings.* It may be desirable to increase the efflux velocity for some reason, for instance to avoid downwash (see 5(v) below). When the plume rises under the influence of buoyancy there is a unique relationship between the velocity, the width of the plume, and the buoyancy. Once this state has been reached the condition of the plume is practically independent of the efflux velocity because the shape of the jet and buoyant plume are so nearly identical. In a jet the velocity decreases more rapidly but the concentration more slowly than in a buoyant plume, so that if there is a large efflux velocity it will decrease until the unique relationship appropriate to a buoyant plume is achieved, and thereafter the motion will be that of a buoyant plume.

An alternative approach is to say that when the upward momentum gained through the action of the buoyancy considerably exceeds that possessed at efflux the latter will not influence the motion. If the density at efflux is $(1-B)$ times that of the surroundings the effluent is subject to a force gB. If w_0 is its efflux velocity, the motion will be that of a buoyant plume at times greater than t after efflux where

$$gBt \geqslant w_0 \tag{1}$$

Because of the smaller velocity the exterior of the jet comes sooner under the control of buoyancy than the central region. In the case of a typical power station chimney this is after 5–10 seconds at most. The mixing of the plume with the surroundings dilutes both kinds of upward momentum equally and does not affect the time t.

On the other hand the narrowing of the nozzle from radius a to radius a' raises the geometrical origin of the cone occupied by the plume by a height h given by

$$\boxed{h = 5(a - a')} \tag{2}$$

because approximately $z = 5r$. In such a case the buoyancy at any level is given by

$$B = B_1(z_1/z)^{5/3} \tag{3}$$

suffix 1 denoting values at any particular level, so that the increase of buoyancy is given by

$$\Delta B/h \simeq \partial B/\partial z = -5B_0 z_0^{5/3}/3z^{8/3} \tag{4}$$

In a typical power station $a = 5$m, $B_0 = (\Delta\rho/\rho)_0 = 0{\cdot}4$, $w_0 = 12$ m/sec, so that if the diameter is halved $a/a' = 2$ and $h = 12{\cdot}5$ m. If we assume that the value of B at the orifice can be inserted in (3) then when $z = 50$ m we find that

$$\Delta B = 0{\cdot}055$$

which corresponds to an excess temperature of about 1·5°C.

In calm surroundings the only purpose of attempting to raise the temperature at any level would be to enable the plume to penetrate a shallow stable layer (or inversion) and in such a case an increase of 1·5°C might be of importance, for whatever the upward velocity of the gases on arriving at a stable layer they cannot rise through it permanently, but must fall back, if they are cooler than the upper layer. If the efflux velocity is raised too much the plume may not have had time to come under the influence of the buoyancy and may still be behaving as a jet on arrival at the stable layer. BOSANQUET has pointed out that if the efflux velocity is increased by narrowing the orifice the concentration is everywhere reduced on account of the increased mixing. If primes denote values for the narrowed orifice at the same height above the apex of the enveloping cone then *in the jet stage*, since the flux of concentration (or of buoyancy) is constant

$$wBz^2 = \text{const. (indep. of height)} \tag{4}$$

The flux of mass is unaltered by narrowing the orifice so that

$$w_0 a^2 = w_0' a'^2, \quad w^2 a^2 = w' a'^2 \tag{5}$$

whence by Table I, column 1, we find that

$$B'/a'^2 = B/a^2 \tag{6}$$

The buoyancy at height H above the narrowed orifice is therefore given by

$$\begin{aligned}(B')_{z=H+5a'} &= \frac{a^2}{a'^2}(B)_{z=H+5a'} \\ &= \frac{a^2}{a'^2}\frac{H+5a'}{H+5a}(B)_{z=H+5a}\end{aligned} \tag{7}$$

This decreases as a/a' increases for all positive values of a/a', so that *an increase of efflux velocity due to a narrowing of the orifice decreases the buoyancy at all levels in the jet stage*.

The height at which the jet stage terminates and above which the motion is controlled by the buoyancy is proportional to $w_0 t$ where t is given by (1) and is therefore proportional to $w_0'^2$, and therefore to a^4/a'^4. If the penetration of a low altitude inversion is the objective care must be taken not to raise the transition height too much by narrowing the orifice.

The additional power required to increase the efflux velocity is not considered here.

(*b*) *Stably stratified surroundings.* The problem of uniform stability has been treated by MORTON (1959). We shall consider two cases of variable stratification which may be of importance. The first is when the lower layers are very stable but

VOL. 1 958/9

the air above is neutral. In such a case an increase in efflux velocity increases the amount of relatively dense air entrained in the lowest levels and therefore decreases the buoyancy higher up. If the stable layers can be penetrated with the smallest possible upward velocity they will arrive in the upper layers with a greater buoyancy and so the ultimate upward velocity attained will be greatest. Ideally the low stable layers should be penetrated without mixing, that is by building the chimney high enough to reach above them (see also 5(iii) below). This situation often arises in the evening and at night.

If the lowest layers are neutral and the upper layers stable, as is often the case when the ground is being warmed in the morning the situation is more like that considered in (*a*) above and too much increase in efflux velocity may be a disadvantage.

(ii) *Decrease of efflux velocity*

When the environment is calm the vertex of the cone enveloping a vertical buoyant plume can be raised by reducing the efflux velocity below that corresponding to the buoyancy. This requires a widening of the orifice, and in order to prevent exterior air from sinking into it the pressure of the effluent at the chimney top must be atmospheric. If primes denote the values to which the orifice conditions are changed, the effluent rises with negligible mixing until the buoyancy has increased the upward velocity to that corresponding to the buoyancy in a hot plume. In the case of no mixing and negligible viscosity the energy equation may be used. The height gained, h, is therefore given by

$$gB_0h = \tfrac{1}{2}(w_0^2 - w_0'^2) \tag{8}$$

But $$w_0' = w_0a^2/a'^2$$

so that $$h = w_0^2(1 - a^4/a'^4)/2gB_0 \tag{9}$$

Approximately, in the turbulent stage of a hot plume

$$w_{max} = 3\overline{w},\ B_{max} = 3\overline{B} \tag{10}$$

and so from Table I we see that, if at the orifice we put

$$\overline{w} = w_0,\ \overline{B} = B_0, \text{ then } 9w_0^2/3gB_0 = (1{\cdot}4)^2 \tag{11}$$

and $$h = \tfrac{1}{6}(1{\cdot}4)^2 z_0(1 - a^4/a'^4)$$

or $$\boxed{h \simeq 1{\cdot}6a(1 - a^4/a'^4)} \tag{12}$$

where a is the radius of orifice at which the buoyancy and velocity are matched as in a buoyant plume. It is seen that this gain in height has an upper limit equal to about one-third of the maximum gain in height due to a decrease in orifice size. This method does not consume any power, but it would be far less effective than calculated if there were a slight breeze.

(iii) *The rise of bent-over jets and buoyant plumes* (Fig. 2)

The rise due to large vertical efflux velocity is regarded as complete when the vertical velocity is reduced to the magnitude of the ambient turbulent velocities which we shall denote by V. Up to this moment the ambient turbulence is assumed to have a negligible effect. After this point the plume is said to become *passive* and is to be treated effectively by theories which consider only the effects of ambient turbulence. In many theories V is assumed to be proportional to the wind U.

The plume becomes bent over when the vertical velocity is small compared with

VOL 1 1958/

the wind. In fact the conversion of a vertical conical jet into a nearly horizontal bifurcated one is gradual, but we shall assume it to take place instantaneously at the height at which the mean upward velocity is equal to μU. μ is about unity.

This treatment of the plume in discrete discontinuous stages is only likely to be valid in cases where the parts of the plume in which transition from one type of motion to another takes place occupy only a small fraction, say less than one-third of the total length considered. Even so each transition is expressed by a disposable

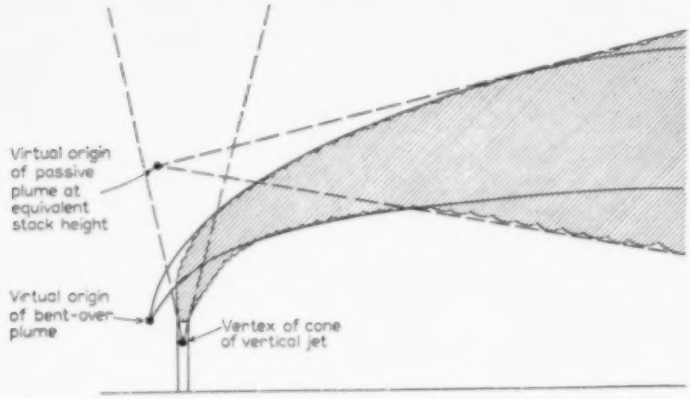
Virtual origin of passive plume at equivalent stack height
Virtual origin of bent-over plume
Vertex of cone of vertical jet

FIG. 2. The bent-over plume or jet is assumed to consist of three parts: a vertical part in which $w>\mu U$, a bent-over part in which $\mu U>w>V$, and a passive part in which $V>w$. Each part has its own virtual origin and the heights of the origins are $z=0$, $y=0$, $z=h+z_0$.

VOL. 1 58/9

constant and this is thought to be as realistic as alternative theories which ignore the differences between the various parts.

There cannot be one law for the dilution in the vertical and bent-over parts of the jet (or buoyant plume), so that any formula must involve μ. We shall assume that the vertical jet and buoyant plume are approximately geometrically similar and heights above the vertex of the enveloping cone will be denoted by z. In the absence of measurements we shall assume that the bent-over jet is similar in section to the bent-over plume and height above their virtual origin will be denoted by y. The height at which $w=\mu U$ will be denoted by z_1 or y_1. Suffix 0 refers to the orifice. In the vertical part we shall assume that the mean upward velocity and buoyancy are $\frac{1}{2}w_{max}$ and $\frac{1}{2}B_{max}$. In the bent-over part the cap of the plume will be assumed to be at height y.

(*a*) *Bent-over jet.* In the vertical part

$$\left.\begin{aligned} w &= w_0 z_0/z\,; \quad \mu U = w_0 z_0/z_1 \\ \sigma &= \sigma_0 z_0/z\,; \quad \sigma_1 = \sigma_0 z_0/z_1 \\ &\qquad\quad = \sigma_0 \mu U/w_0 \end{aligned}\right\} \tag{13}$$

The flux of pollution is equal to

$$\sigma_0 w_0 \pi a^2 = F \tag{14}$$

In the bent-over part the flux is $2{\cdot}5r^2\sigma U$ because the horizontal velocity is approximately that of the wind. But $r=y/2{\cdot}25$ and so, since the flux is constant,

$$2{\cdot}5(y_1/2{\cdot}25)^2(\sigma_0\mu U/w_0)U = \sigma_0 w_0 \pi a^2 \tag{15}$$

and so
$$y_1 = 2{\cdot}25(\pi/2{\cdot}5\mu)^{\frac{1}{2}} w_0 a/U \tag{16}$$
Since σ and w are proportional throughout, the flux of upward momentum is also seen to be preserved. In the bent-over part
$$w = w_1 y_1^2/y^2 \tag{17}$$
so that the height at which the plume becomes passive is
$$\begin{aligned} y_v &= y_1 (w_1/V)^{\frac{1}{2}} \\ &= 2{\cdot}25(\pi/2{\cdot}5\mu)^{\frac{1}{2}} (w_0 a/U)(\mu U/V)^{\frac{1}{2}} \end{aligned} \tag{18}$$
If we put $V = \lambda U$, where in practice $\lambda = 0{\cdot}1$ or thereabouts, then
$$y_v = 2{\cdot}25(\pi/2{\cdot}5\lambda)^{\frac{1}{2}} w_0 a/U \simeq 2{\cdot}5 a w_0/\lambda^{\frac{1}{2}} U \tag{19}$$
The total rise h from the orifice is therefore (with $z_0 = 5a$)
$$\boxed{h = y_v - y_1 + z_1 - z_0 = 2{\cdot}5a\left\{\frac{w_0}{U}\left(\lambda^{-\frac{1}{2}} - \mu^{-\frac{1}{2}} + 2\mu^{-1}\right) - 2\right\}} \tag{20}$$
Since μ is of the order of unity $2\mu^{-1} > \mu^{-\frac{1}{2}}$. If the orifice radius is reduced to a', by (5)
$$w_0' a' = w_0 a \frac{a}{a'} \tag{21}$$
and so the value of h in (20) is only decreased if
$$w_0(\lambda^{-\frac{1}{2}} - \mu^{-\frac{1}{2}} + 2\mu^{-1}) < 2U \tag{22}$$
But λ is of the order of 10^{-1} and μ is of the order of unity and so (22) is unlikely to hold.

(*b*) *Bent-over buoyant plume.* If we suppose first that the buoyancy has a negligible effect until after the plume is bent over then in the bent-over part
$$\left.\begin{aligned} B &= B_1 y_1^2/y^2 \\ r &= y/2{\cdot}25 \end{aligned}\right\} \tag{23}$$
and
$$\begin{aligned} w &= 0{\cdot}8(gBr)^{\frac{1}{2}} \\ &= 0{\cdot}8(gB_1/2{\cdot}25y)^{\frac{1}{2}} y_1 \end{aligned} \tag{24}$$
But
$$B_1 = B_0 \mu U/w_0 \tag{25}$$
and so the plume becomes passive where $y = y_v$ given by
$$V^2 = (0{\cdot}8)^2 g B_1 y_1^2/2{\cdot}25 y_v \tag{26}$$
i.e.
$$\begin{aligned} y_v &= g B_0 w_0 \pi a^2 (0{\cdot}8)^2 2{\cdot}25/2{\cdot}5 U V^2 \\ &= 0{\cdot}58 F/UV^2 \end{aligned} \tag{27}$$
which is independent of μ. F is the flux of buoyancy from the orifice, and is equal to $\pi a^2 w_0 (\Delta\rho/\rho)_0$. If $V = \lambda U$ the total rise is
$$\boxed{\begin{aligned} h &= 0{\cdot}58 F/\lambda^2 U^3 - y_1 + z_1 - z_0 \\ &= 0{\cdot}58 F/\lambda^2 U^3 + 2{\cdot}5a\left\{\frac{w_0}{U}\left(-\mu^{-\frac{1}{2}} + 2\mu^{-1}\right) - 2\right\} \end{aligned}} \tag{28}$$
This formula only applies if the buoyancy becomes active before the plume

becomes passive, i.e. if equation (27) gives a greater value to y_v than (18), or, when $V=\lambda U$

$$F > \frac{2{\cdot}5}{0{\cdot}58} a w_0 \lambda^{3/2} U^2 \tag{29}$$

or
$$gB_0 > \frac{2{\cdot}5}{\pi} \frac{2{\cdot}5}{(0{\cdot}8)^2 2{\cdot}25} \frac{\lambda^{3/2} U^2}{a} = 1{\cdot}4 \lambda^{3/2} U^2/a \tag{30}$$

Greater buoyancies than this contribute to the plume rise. It is interesting that this condition is independent of μ and does not appear to be influenced by the bending-over mechanism.

In equation (26) the term containing λ is now independent of a and w_0, and is unaffected by change in orifice size. But when

$$w_0(-\mu^{-\frac{1}{2}} + 2\mu^{-1}) < 2U$$

or roughly when
$$w_0 < 2U$$

and the buoyancy is large enough for (29) and (30) to hold, a decrease of orifice size decreases the value of h given by (28), in conformity with BOSANQUET's similar result. For larger values of w_0 narrowing of the orifice increases h, but for the increase to be substantial the increase in aw_0 must be large in practical terms because the actual amount of the second term in the right-hand side of (28) is not great. The raising of h is achieved by raising the point of bending over and this is so near to the chimney mouth in average conditions that the narrowing is scarcely worth-while.

When $w_0 < 2U$ the point of bending over is not raised by increasing the efflux velocity because of the increased rate of dilution.

(*c*) *Bent-over plumes of large buoyancy.* Larger buoyancies may contribute to the rise before the plume becomes bent over. In that case in the vertical part we have by (10)

$$3w = 1{\cdot}4(g3Bz)^{\frac{1}{2}} \tag{31}$$

or
$$w^2 = \tfrac{8}{3} gBz \text{ approximately,} \tag{32}$$

But
$$F = gB_0 w_0 \pi a^2 \tag{33}$$

and if the motion is that of a vertical buoyant plume from $z = z_2 < z_1$ upwards

$$F = n\pi r^2 wgB \tag{34}$$

where n is a number depending on the spatial and temporal correlation between vertical velocity and buoyancy fluctuations which will cause the flux to exceed that given by the mean values. Also B is given by (32) and so z_1 is given by

$$F = n\pi \left(\frac{z}{5}\right)^2 w \frac{3w^2}{2z}$$

$$= 3n\pi z_1 \mu^3 U^3/50 \tag{35}$$

i.e.
$$z_1 = 50F/3n\pi\mu^3 U^3 \tag{36}$$

By Table 1, column 2, top line,

$$3\mu U = 4{\cdot}7 z^{-\frac{1}{2}} F^{\frac{1}{2}} \tag{37}$$

and so

$$z_1 = \frac{(4{\cdot}7)^3 F}{27\mu^3 U^3} \simeq 3{\cdot}8F/\mu^3 U^3 \tag{38}$$

VOL. 1 58/9

Comparing this with (36) we find that $n \simeq 1{\cdot}4$, which is reasonable, and the assumption (10) therefore also seems reasonable. Then

$$gB_1 = 3w_1^2/2z_1 = 0{\cdot}39\mu^5 U^5/F \tag{39}$$

On bending over the flux of buoyancy is conserved, so that

$$F = 2{\cdot}5\left(\frac{y_1}{2{\cdot}25}\right)^2 gB_1 U \simeq \frac{0{\cdot}39 \times 2{\cdot}5}{(2{\cdot}25)^2} y_1^2 \frac{\mu^5 U^6}{F} \tag{40}$$

and

$$\left.\begin{aligned} y_1 &= \frac{2{\cdot}25F}{(2{\cdot}5 \times 0{\cdot}39)^{\frac{1}{2}}\mu^{5/2}U^3} \simeq \frac{2{\cdot}25}{\mu^{5/2}}\frac{F}{U^3} \\ \text{and} \qquad gB_1 y_1^2 &= \frac{(2{\cdot}25)^2}{2{\cdot}5}\frac{F}{U} \end{aligned}\right\} \tag{41}$$

After bending over there will be a short length of bent-over jet in which the upward velocity will get reduced to that of a bent-over plume with the actual buoyancy possessed by it. Thereafter the motion will be as in the bent-over plume in which the value of y_1 given in (41) is substituted for that in (16). But substituting for $gB_1 y_1^2$ in (24) we again obtain (27) for y_v. But the total rise is now (with $V = \lambda U$) obtained using (41). Thus

$$\boxed{\begin{aligned} h &= y_v - y_1 + z_1 - z_0 \\ &= \left\{\frac{0{\cdot}58}{\lambda^2} - \frac{2{\cdot}25}{\mu^{5/2}} + \frac{3{\cdot}8}{\mu^3}\right\}\frac{F}{U^3} - 5a \end{aligned}} \tag{42}$$

In this case a decrease in a necessarily increases h.

This formula applies instead of (28) only if the second term is greater, i.e. when the buoyancy becomes effective in the vertical part. This happens if

$$\frac{2{\cdot}25}{\mu^{5/2}}\frac{F}{U^3} > \frac{5w_0 a}{\mu U}. \tag{43}$$

or

$$F > \frac{5\mu^{3/2}}{2{\cdot}25} w_0 U^2 a \simeq 2{\cdot}2\mu^{3/2} w_0 U^2 a \tag{44}$$

or

$$gB_0 > \frac{5\mu^{3/2}}{2{\cdot}25\pi}\frac{U^2}{a} \simeq 0{\cdot}7\mu^{3/2}U^2/a \tag{45}$$

In equation (42) the third term is about 1·7 times the second so that there is always a gain from increased buoyancy.

In comparing (42) with (28) the question arises whether by an increase in w_0 such as to replace (42) by (28) and make (44) invalid the total rise can be reduced: according to the present theory this could not be so.

In all these formulae μ is around unity and the effective height is the stack height $+ h$.

In the case of washed plumes the problem is complicated by the release of negative buoyancy as the dilution proceeds, but it seems likely that any increase in efflux velocity due to narrowing the orifice will reduce the effective stack height by bringing forward the moment from which this large negative buoyancy operates.

VOL 1 1958

VOL.
1
58/9

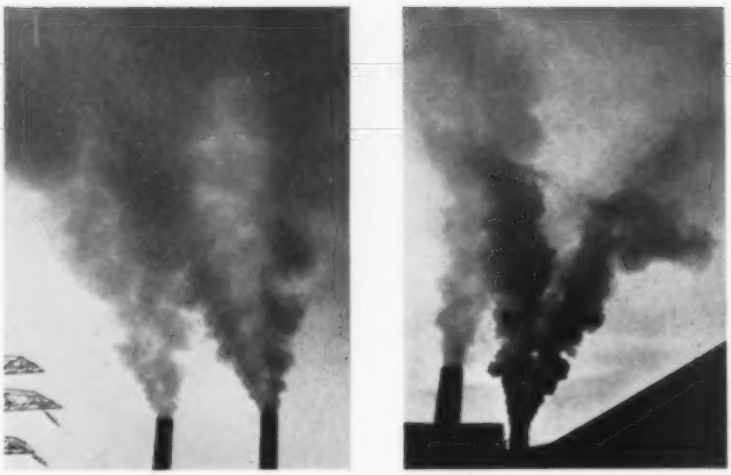

FIG. 3. Bifurcation by buoyancy of the plumes at Keadby (near Scunthorpe) power station (left) and Battersea power station (right), seen from underneath in a moderate wind.

VOL
1
1958

5. SOME SPECIAL PROBLEMS

(i) *The settling of dust out of a plume*

It has generally been supposed that grit and dust will settle out of a plume with its terminal velocity. It might alternatively be argued that " turbulence " within a hot plume would delay the fall-out of *some* particles by diffusing them upwards. In a bent-over plume in which the buoyancy produces an effective upward velocity there is an ordered motion of the type shown in Fig. 1. The rising gases increase in volume both by mixing with the air into which they ascend and by an ordered entrainment of exterior air into the bottom of the plume. The plume thus becomes bifurcated (Fig. 3). The consequence of this entrainment is that many particles which have fallen out of the plume are absorbed into it again.

WOODWARD (1959) has measured the velocity distribution in and around a thermal (see also SCORER 1958) and has found that if w_c is the upward velocity of the uppermost part of the thermal, particles whose terminal velocity is less than about $0{\cdot}4w_c$ cannot fall out, and that only particles whose terminal velocity exceeds about $1{\cdot}6w_c$ must fall out. Some of the particles of intermediate size are retained and some fall out according to their position within the thermal. It is reasonable to suppose that a similar study of a bent-over plume (or cylindrical thermal) would show that the corresponding particle fall speeds would be of about the same magnitude. Because the cylindrical thermal is decelerated more slowly than one symmetrical about a vertical axis the phenomenon of entraining fall-out is probably more important than in the isolated thermal studied by WOODWARD.

The consequence is that the smaller particles are carried much further from the chimney in light winds than simpler theories have suggested, because the fall speeds are not normally much in excess of the rate of rise of the plume. They are probably spread over 2 or 3 times the area computed without taking this into account in air of small ambient turbulence, which is the important case.

It is equally difficult for buoyant particles to emerge from the top of a bent-over plume because of the mixing with the air into which the plume is rising. LUCAS, SPURR, and WILLIAMS (1957) found that balloons sent up a power station chimney almost invariably remained within the plume delineated by smoke, and this is almost certainly because they never acquired a sufficient weight deficiency or excess to acquire a velocity relative to the air comparable with the upward velocity of the plume. No computations of the speed of free ascent required to escape have been made for a thermal, but a cursory examination of the rapid decrease in the velocity of the air above a thermal shows that it must be of the order of $\frac{1}{2}w_c$.

(ii) *The production of thermals*

In order to produce thermals a source of heat must be comparable with the power of sunshine received over an area which normally supports a thermal. Sunshine is variable in angle of incidence and in intensity on account of thin or dense cloud, and the fraction of it converted into sensible heat in the air depends mainly upon the rate of evaporation of water at the ground. Assuming a typical figure of around 10^7 ergs cm^{-2} min^{-1} the heating power of sunshine over a 500 m square is about 40 MW. It is known from glider pilots' experience that thermals are produced over concrete runways whose area is this order of magnitude. A typical power station chimney supplies 50 MW as heat so that thermals are easily produced. The pollution is then

VOL. 1 958/9

carried up to the height reached by thermals, which for most thermals is about the height of cloud base—say 1000 m, after which it may be diluted downwards by the ambient turbulence. The concentrations experienced at the ground will be negligible compared with those produced by sources of pollution not producing thermals.

(iii) *Smoke plumes in valleys*

When the winds are light the air in a valley becomes stably stratified, especially at night and particularly in winter. During long nights the pollution emitted at 100 m

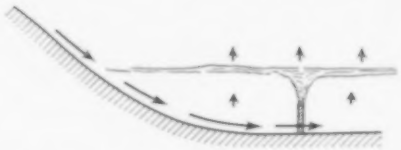

FIG. 4. The nocturnal circulation in a valley which brings smoke down the hillsides after it has spread out horizontally in a stably-stratified atmosphere.

above the valley floor may be mixed down to the valley bottom by the drawing of cold air down the hillsides (Fig. 4).

During the day most of the air often remains stably stratified while warm air flows up the hillsides, receiving heat from them as it ascends. This means that when the smoke can be seen to have been mixed up to a height of 500 m the warm gases from a 100 m chimney may yet rise only another 50–100 m before levelling out, and the hill-

FIG. 5. The daytime circulation in a valley which carries pollution from a chimney up to a haze top in a stable atmosphere after it has spread out at a lower level.

sides just above chimney-top level may be seriously polluted. There will even be pollution at the foot of the chimney (Fig. 5). The only satisfactory way of preventing all the ground in the valley from being polluted on such occasions is to have the chimney top so near to the valley top that the gases rise above the very stable layer. Provided that the plume can ascend above the hillsides the problems peculiar to a valley will not arise.

(iv) *Eddies in the lee of cliffs*

In the lee of a cliff there may be eddies, either steady or unsteady, of the kind shown in Fig. 6. If a chimney is sited in the downdraught of the eddy the plume may be carried down to the ground bodily, which is more serious than being diffused down by ambient turbulence. The chimneys at Hope cement works near Sheffield behaved in this way (see Fig. 7) while at other times the pollution accumulated under a stable layer (see Fig. 8). Both these problems were virtually solved by installing a 150 m chimney which reaches above the eddies, and is so near to the valley top that most stable layers are penetrated by the hot plume in light winds.

VOL 1 1958/

FIG. 7. The smoke from Hope cement works carried down to the ground where the flow returns to the surface at the lee of an eddy behind a hill (see Fig. 6). The black smoke trail is from a generator on the cable of the tethered balloon.

Photo by A.P.C.M. Ltd. Research Department.

VOL.
1
58/9

FIG. 8. The buoyant plume from Hope cement works, near Sheffield, sinking back after arriving at a "discontinuity" of temperature with an upward velocity but with insufficient buoyancy to penetrate it permanently.

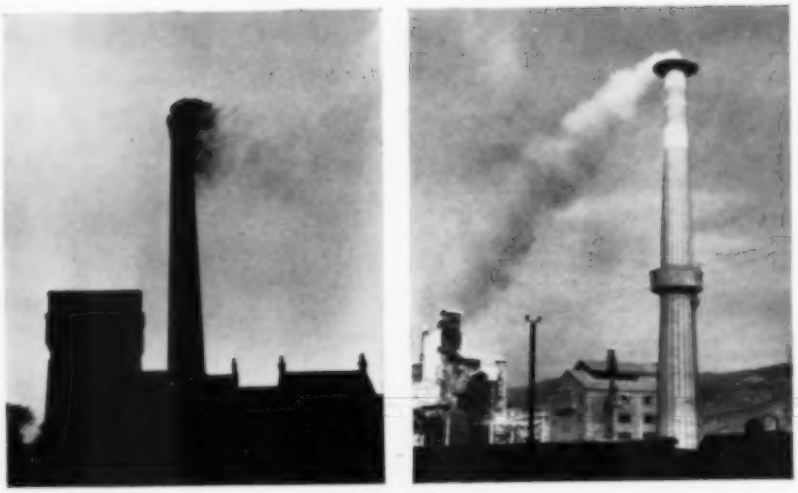

FIG. 9. The disc on the top of a chimney at St. Auban sur Durance, France, installed to prevent downwash of the kind illustrated in the left-hand picture.

VOL
1
1958/

(v) *Downwash*

Downwash is the entrainment of effluent into the immediate lee of the chimney. It causes blackening. The effluent has been known to erode concrete chimneys on the outside when downwash occurs. It can be prevented by increasing the efflux velocity to about the magnitude of the wind velocity, or greater. The precise velocity

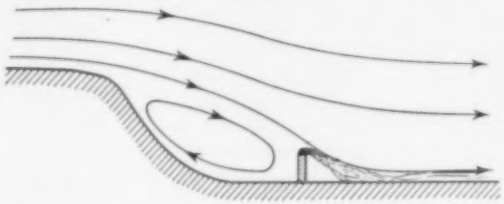

FIG. 6. Smoke from a chimney carried directly down to the ground if the chimney is at the point where the flow rejoins the ground at the lee side of an eddy after separating at a cliff top.

necessary depends upon the shape of the chimney top. Buoyancy has a negligible effect because the entrainment occurs too soon after efflux.

Downwash may also be avoided by placing a horizontal disc (see Fig. 9) at the chimney top. Standing eddies are not larger than the chimney. Therefore if the disc extends outwards one chimney diameter all round, any effluent entrained into eddies will be carried away by the wind because the eddies there will be moving.

6. POLLUTION BY PASSIVE PLUMES

When the equivalent stack height has been decided, a method must be devised for determining the pollution at the ground. It is not considered worth-while to derive a formula except for neutrally stable air because the variation in stability with height can produce over-riding effects. Some attempts have been made to give formulae which will apply when there is a uniform temperature gradient; but uniform gradients (other than that corresponding to neutral stability) and, therefore, the circumstances in which the formulae would apply, are so rare that they have no practical utility.

The difficulties are even greater when the wind is very light or calm or when the pollution is falling out or is being absorbed on to fog droplets which, in turn, fall out at a rate comparable with the rate of supply. And even if formulae could be devised to predict such phenomena as the accumulation of smoke in a shallow layer at a small distance (say, between 10 and 30 m) above a datum level so that the concentration varies greatly with the topography, they would have little use because the temperature varies with time of day often quite rapidly in such circumstances, so that the behaviour of the pollution depends not only on the present conditions but also on its past history.

Therefore, rather obvious simple formulae cannot be improved upon. The simplest is that the pollution is carried down a cone with vertex at the equivalent stack height above the chimney. On reaching the ground the pollution must be computed on the assumption that an image source exists below ground. The profile of concentration across the cone may be taken in *any* form convenient to the case. None of the commonly used profiles such as circular, parabolic, wedge-shaped top-hat, or Gaussian has any over-riding merit. The half-angle of the cone is not a

VOL. 1 58/9

universal constant because slight departures from neutral stability can alter it greatly but it is generally between 10° and 20°.

In all cases there are two well-known results:

$$P \propto 1/U$$

where P is the pollution and U the wind speed, and

$$P \propto 1/h^2$$

where h is the equivalent stack height. The first follows because the amount of pollution carried away does not depend on the wind. The profile of pollution across plume and the plume width do not vary primarily on account of wind speed: in ideal turbulent conditions, it must be independent of it because all turbulent velocities would be proportional to the wind and the geometry of the flow would be independent of speed. The second result depends upon the similarity of the plume at all distances and is only true in a special sense. For instance, the nearest polluted point is at a distance x proportional to h and the amount of pollution there is proportional to $1/x^2$. The decrease of pollution at a point on the ground resulting from an increase in stack height depends upon the profile across the plume. But the contours of pollution have the same shape and size when drawn using the equivalent stack height as unit of length and the pollution itself on such a map is proportional to $1/h^2$.

If the pollution is confined below a temperature discontinuity, after the cone has reached up to the discontinuity, the spreading is sideways only. Consequently, the pollution decreases thereafter only like x^{-1} and soon becomes independent of height except at the sides of the plume.

For purposes of computing the pollution in a large city due to various sources simple formulae of this kind can be used with as much confidence that they represent reality as any of the more sophisticated formulae: but the same cannot be said of the transfer of heat and momentum because they affect the motion in an important way. A theory of heat transfer may be used for pollution in the same air: but we may make a reasonable estimate of passive pollution with formulae which cannot be usefully applied to heat and momentum and we need not wait for a theory which can be so applied.

Sometimes when there is a dense accumulation of pollution and very frequently when there is a wet fog the layer containing it is neutrally stratified and has a stable discontinuity of temperature at the top. Particularly in calm conditions there may be convection downwards from the top which is losing heat by long wave radiation into space. Hot plumes from large chimneys then flatten out at the top and are gradually diffused downwards. A slight wind may be sufficient to carry them a few miles before there is pollution at the ground: but when there is no motion of the air as a whole, the pollution is accumulated and only a decrease of output or natural removal by falling out can reduce concentrations. Under such circumstances, the washing of effluents may be valuable but its merit is in serious doubt at all other times because of the cooling due to the added liquid water.

7. PLUMES CONTAINING LIQUID WATER

In any wet flue gas-washing process, the gases are cooled and almost certainly become saturated. The temperature at which they become saturated in the presence of water is approximately their wet-bulb temperature before the beginning of the

process and the cooling down to this temperature is affected primarily by the evaporation of water into the gases. After the gases are saturated they may be cooled further by contact with cold surfaces, either liquid or solid, and the cooling is distributed throughout the volume of the gas by turbulent mixing in such a way that liquid water is condensed in the form of cloud particles and is not deposited in comparable amounts on to the cooling surfaces. The cloud particles are sufficiently small generally to avoid capture and they emerge from the chimney top. In such a case the significant temperatures are the wet-bulb temperature of the original flue gases and their temperature at efflux. If these are given, the amount of liquid water suspended in the effluent can be computed from Table 2 which gives the amount of water-vapour, in grammes, mixed with 1 kg of dry air at various temperatures when the mixture is saturated. The amount condensed as cloud is the difference between the amounts of vapour present at the two temperatures.

TABLE 2. AMOUNT OF WATER MIXED WITH 1 kg OF DRY AIR AT VARIOUS TEMPERATURES WHEN THE AIR IS SATURATED AT 1000 mb

Temp (°C)	10	15	20	25	30	35	40	45
Water-vapour (g)	7·7	10·8	14·9	20·3	27·6	37·1	49·5	65·9
Temp (°C)	50	55	60	65	70	75	80	85
Water-vapour (g)	876	116	155	208	282	390	560	852

VOL. 1 58/9

Steam locomotives also emit condensed water in the form of cloud droplets. In this case the condensation occurs when the steam expands almost adiabatically and is thereby cooled.

The flue gases from cement kilns using raw material in the form of a slurry also contain a large amount of water-vapour and some of this may be condensed as cloud before emergence at the chimney top.

After emission, there may initially be some further condensation as in aircraft condensation trails, when the effluent is mixed with unsaturated surrounding air at a much lower temperature. In such a case there is a gain of heat by the plume but this is subsequently lost again, generally in a few seconds, when the cloud evaporates as the mixing continues. The beneficial effect of this temporary borrowing of heat from the water may occasionally be important but it will not be considered here. Much more important is the loss of heat which occurs when the water which emerged in liquid form is evaporated.

The heat lost in the evaporation of 10 g of liquid water is sufficient to cool 1 kg of air by 25°C approximately. The dilution very quickly becomes many-fold so that it is most profitable to consider the cooling produced in 100 times the volume emerging from the chimney. Fig. 10 shows the magnitude of it. It will be seen that, in a typical case of flue gases having a wet-bulb temperature of 60°C and emerging at 30°C after wet washing, the evaporation of the liquid water will cool the whole by 3·2°C after it has been diluted 100 times. Alternatively, we may say that it will behave from then onwards in the same way as a plume emerging with a temperature about 320°C less than that of the actual plume. Fig. 11 shows how it could be considered as emerging from a higher orifice than the actual plume and behaving roughly as a plume with negative buoyancy. Since wet-washed plumes generally

emerge only slightly warmer than the surroundings and certainly with an excess of a smaller order than 100°C, the cooling due to the condensed water usually far outweighs the buoyancy due to water-vapour or excess temperature, or the negative buoyancy of carbon dioxide.

On account of this effect, the plumes from the power stations at Battersea and

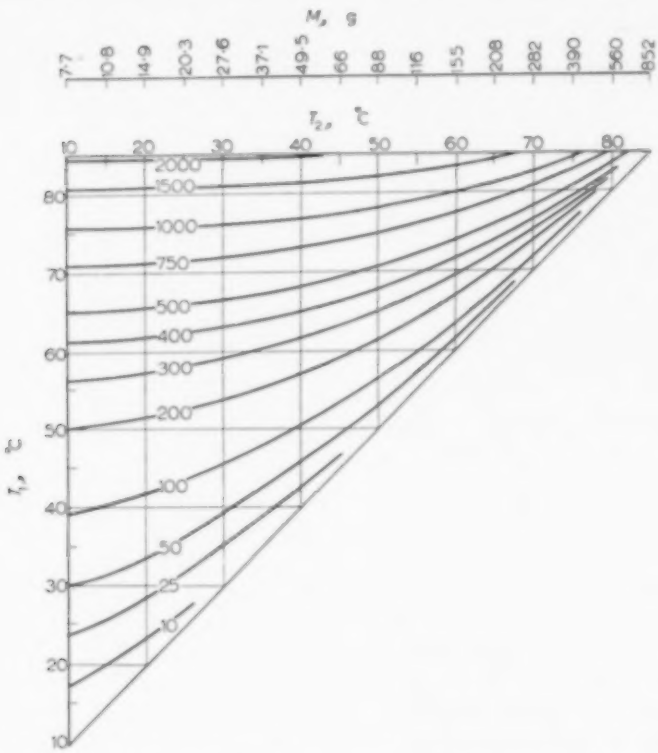

FIG. 10. The cooling of the plume due to the evaporation of water condensed in it before efflux. T_1 is the temperature at which the gases are saturated. T_2 is the temperature at which they emerge. The isopleths show the amount in °C by which the original effluents would have had to be cooled to produce a plume with the same temperature as that possessed by the actual plume after the water has evaporated. More realistically the figures could be taken to indicate the factor by which the effluents must be diluted for them to suffer a drop of 1°C on account of the evaporation.

Bankside in London can almost invariably be seen to obscure the chimney tops when viewed from ground level more than about a quarter of a mile downwind. Plumes with such a large negative buoyancy would have a negative equivalent stack height if the concept were strictly applied and it is not surprising that the plumes usually reach the ground within a few hundred yards of the chimney when ambient turbulence is not large.

At cement works the problem is generally of minor importance. The cooling occurs in the precipitators and in the chimney, mainly by conduction through the walls. In winter a typical plume emerges white and containing cloud, indicating that it has been cooled to below its dewpoint. But, in summer, many plumes show a

transparent region close to the stack mouth and the condensation only occurs after some mixing with the surrounding air.

The effluent from a steam locomotive might perhaps be half water-vapour. It would, in that case, be saturated at about 79°C. If it is cooled by the expansion to about 60°C, the evaporation of the water condensed would cool the plume when mixed with 100 times its mass of surrounding air, by about 10°C. Consequently, it is common to see the effluents descend to the ground beside a railway train, obscuring

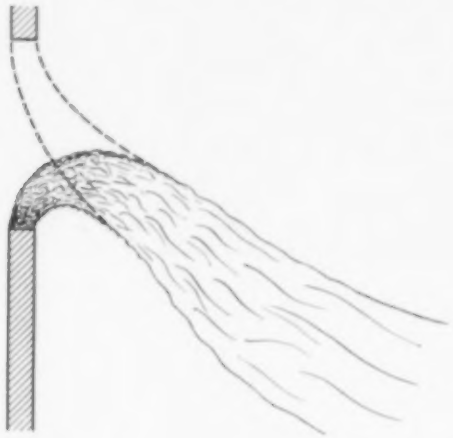

FIG. 11. After the evaporation of all the liquid water a cold plume behaves like one with negative buoyancy emerging from an orifice at a greater height than the actual one. The temperature deficit of the equivalent plume at the higher orifice is given by Fig. 10.

VOL. 1 58/9

the passengers' view. On occasions when I have noticed the condensation occurring after emergence from the locomotive chimney I have not noticed any marked tendency for the plume to sink to the ground.

These effects of evaporation have not been taken into account in any of the published computations of pollution from a power station chimney emitting wet-washed gases. It is clear that a computation based on an equivalent stack height must fail and that the negative buoyancy is enough to be of major importance on an ordinary day just as positive buoyancies of similar magnitude serve to double the effective stack height. Moreover, on occasions when the ambient turbulence is slight, such as that illustrated in Fig. 12, the effect is over-riding and even when the atmosphere below chimney top is stably stratified, as it often is in an evening, the plume may still descend to the ground when no other pollution from tall chimneys is carried downwards at all.

8. THE PROBLEM OF THE ARCHITECT

The title of this section is deliberately ambiguous for not only have the architects a problem in designing chimneys which blend unobtrusively with the rest of their plan, but engineers also have a problem in persuading the architect to take chimneys seriously. Evidently many architects are not convinced that a chimney which satisfactorily removes the pollution must be obtrusive. If fuel is burned within a building,

the chimney is a functional part of it. Nineteenth-century industrial architects were concerned often to decorate a tall chimney which was required to produce a strong draught. Others have hidden the chimneys of their heating plants within towers (e.g. Cambridge University Library and Natural History Museum, South Kensington and the result is often to suggest that the fire is part of a rite being performed within, as in a crematorium). Often the chimneys have been hidden behind a pitched roof (as at many power stations of the 1930's in Britain and many pseudo-Georgian residential buildings, such as the new University Hall of Residence at Pantycelin, Aberystwyth) with the result that the roof and upper stonework has been rapidly blackened and the smoke is often carried down to the ground in the immediate neighbourhood of the building. The $2\frac{1}{2}$ times rule which is designed to prevent this, and has been freely applied in modern power stations where the chimney is essential to the basic purpose of the building, cannot be applied to blocks of flats and civic buildings and many architects have still tried to have no chimney visible.

Faced with the problem of pollution over the surface of the building, architects reluctantly allow the chimneys to protrude but never as far as is necessary. Often irrelevant shapes are used, such as that shown in Fig. 13. This attempts to pretend that the chimney is really an empty vase. The chimney widens the orifice so that the efflux velocity is very small; consequently, downwash occurs and, in a few weeks, the chimney has become blackened. This blackening was not in the original plan but is as much a reality as the chimney shape. An imaginative and well-informed architect might have employed a disc at the chimney top (see Fig. 9) both to prevent the downwash and to devise a shape in keeping with the building.

In plans chimneys are usually without plumes. Cement works almost always emit white ones which are as important as the chimneys to their appearance. In the case of the works at Hope, mentioned above, objectors to the chimney for aesthetic reasons obtained a ruling that the chimney should not protrude above the skyline, with the result that it was built 50 ft smaller than the engineers asked for. The works operates continuously, so that the white plume is almost always visible above the skyline. Pollution on the neighbouring hillsides is inevitably greater than if the chimney had been allowed to protrude. If aesthetic considerations include the prevention of litter, do they not also require that there should be no smells?

Another case in which superficial aesthetic arguments have over-ridden sound engineering is Bankside power station. Because of the possible pollution in the City of London, gas washing was required. This resulted in the plume being dense white on account of the liquid water contained in it. In order that the chimney should not stand above St. Paul's Cathedral its equivalent height was raised by narrowing the orifice. As seen, the chimney generally sends its dense plume well above St. Paul's so that the Cathedral does not, after all, dominate the skyline. It is doubtful whether the pollution has been reduced by the washing because of the subsequent descent induced by the evaporation. A hot, almost invisible plume would not have added to the appearance of the chimney height and the equivalent height would have been greatly increased on almost all occasions when pollution is serious. The value of the washing is, therefore, questionable on aesthetic grounds. Even if harm done by the sulphur put into the river is ignored, it has been forcibly argued (SCORER, 1956) that gas washing is economically unsound.

Foul air and blackened buildings are out of keeping with this sanitary age. We

VOL
1
1958/

FIG. 12. The washed plume at Battersea, London, brought down to the ground so as temporarily to obscure the power station from view.

VOL.
1
58/9

FIG. 13. A chimney on a new block of flats at Roehampton, England, designed to look like something else, but betraying its true nature by blackening the concrete.

VOL
1
1958/

have a problem in that architects are evading, not solving, the problem posed by the necessity for tall chimneys.

Acknowledgement—I am indebted to Dr C. H. BOSANQUET for several valuable comments on an earlier draft of this paper.

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APPENDIX

Examples in the Use of the Formulae

For the sake of argument we shall assume to begin with that

$\mu = 1$	(the plume becomes bent over when the upward speed is decreased to the wind speed)
$\lambda = 10^{-1}$	(the turbulent velocities are about a tenth of the wind speed)
$w_0 = 10^3$ cm sec^{-1}	(the efflux velocity is about 30 ft/sec)
$a = 500$ cm	(the chimney diameter is about 30 ft)
$U = 5 \times 10^2$ cm sec^{-1}	(the wind speed is about 15 ft/sec)

These would be typical values for a large industrial chimney on a day of light–moderate wind. We shall write $g = 981 \simeq 10^3$ cm sec^{-2}.

Example (*i*)

Equation (1) states that the buoyancy becomes dominant over any effects of velocity of efflux when

$$gB_0 t \gg w_0$$

For an efflux buoyancy of about 0·3, i.e. an excess temperature of about 100° C for gases of density about the same as air at the same temperature, we have

$$t \gg 1/0{\cdot}3$$

and so for times much in excess of about 5 sec the buoyancy is dominant in producing plume rise. The buoyancy is important if the effluent becomes passive more than 5 sec after efflux.

Example (*ii*)

Equation (45) gives the condition for the buoyancy to become effective before the plume becomes bent over. In the example under consideration this gives

$$B_0 > 0{\cdot}7\mu^{3/2}U^2/ga = 0{\cdot}7 \times 1 \times 25 \times 10^4/10^3 \times 500$$
$$= 0{\cdot}35$$

For gases with composition like air the excess temperature must therefore exceed 0·35 times the absolute temperature. For air at 290° K the excess temperature must be more than about 100° C.

VOL. 1 58/9

But this consideration is only important if z_1 (the height at which the buoyancy becomes dominant) $> z_0$, i.e. by (38) if

$$z_1 = 3{\cdot}8F/\mu^3U^3 > 5a \ ;$$

otherwise the plume, which is presumed to have come from a point source, will reach the height z_1 *before* emerging from the orifice. If $B_0 = 0{\cdot}5$ then

$$F = \pi a^2 w_0 B_0 \simeq 4 \times 10^8 \text{ cm}^3 \text{ sec}^{-1}$$

(Strictly F should be decreased in the ratio $1/(1+B_0)$ because in our case for a given w_0 the mass flux is decreased in this ratio, but this effect is small.)

Thus

$z_1 \simeq 15 \times 10^8/U^3$ when $\mu = 1$

$> 5a$ for the buoyancy to be important before bending over occurs.

i.e. $U^3 < 3 \times 10^8/a = 0{\cdot}6 \times 10^6$ in our case

i.e. $U < 83$ cm sec^{-1}

For greater values of U it does not matter what happens before the plume becomes bent over, and in equations (28) and (42) the dominant term is $(0{\cdot}58/\lambda^2)F/U^3$. If $U = 5 \times 10^2$ cm sec^{-1} this term is equal to about 190 cm with the above value of F, which is less than $5a$, and so in fact the plume would be passive from the orifice.

However, this term depends on λ^{-2} and U^3, so that for lighter winds and less turbulence the buoyancy quickly becomes important. Thus if we imagine an evening of light winds when $\lambda = 2 \times 10^{-2}$, and $U = 2 \times 10^2$ cm sec^{-1}, such as would be the case as the air became stabilized below chimney-top level when the ground cooled, then

$$h \simeq \frac{0{\cdot}58}{\lambda^2}\frac{F}{U^3} - 5a = \frac{0{\cdot}58 \times 4 \times 10^8}{4 \times 10^{-4} \times 8 \times 10^6} - 2500 \text{ cm}$$

$$\simeq 7 \times 10^4 \text{ cm} \quad = 700 \text{ m} \simeq 2000 \text{ ft.}$$

This indicates how crucial the meteorological conditions are in determining whether the buoyancy is effective or not. It explains why a power station plume can be carried almost horizontally in the afternoon but may rise up to form clouds in the evening.

Example (iii)

When the flux of buoyancy is small the terms in w_0/U which were negligible in the last example may be important in light winds or when the efflux velocity is large. Thus if there is a converging nozzle at the chimney top (as at Bankside power station) so that $a = 250$ cm and $w_0 = 4 \times 10^3$ cm sec^{-1} (about 120 ft/sec), then if $U = 10^2$ cm sec^{-1}, $\mu = 1$, and $F = 0$, equation (20) gives

$$h = 2{\cdot}5 \times 250 \left\{\frac{4 \times 10^3}{10^2}(\lambda^{-1/2} - 1 + 2) - 2\right\}$$

$$= 240 + 250\lambda^{-1/2} \text{ m.}$$

This can be a very considerable height when λ is of the order of 10^{-1}. On a day of thermal convection and light winds λ might be of the order of unity; but on occasions when λ is of the order of 10^{-2} there is usually slight stable stratification near to the ground which might be important when there is no buoyancy, but not with a buoyancy of the magnitude considered in example (ii).

It is noteworthy that a decrease in turbulence (decrease in λ) gives a much greater increase in plume rise when there is buoyancy (λ^{-2} in equations (28) and (42)) than when there is none ($\lambda^{-\frac{1}{2}}$ in (20)).

At Bankside such heights are never realized because of the negative buoyancy produced by evaporation of the liquid water in the plume.

Comment

Ordinary variations in λ and U can alter the equivalent stack height by an order of magnitude. The maximum ground pollution is inversely proportional to the square of this height in a neutral atmosphere, while there may be no pollution at all if a stable layer is penetrated. The pollution may be independent of stack height if it is trapped below a stable layer. A single formula used by engineers in stack " design " must be treated as convenient for design purposes but not relevant to reality.

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DETERMINATION DE LA POLLUTION DE L'AIR ET DE L'IRRADIATION AU SOL, DUES AU "PANACHE" D'UN REACTEUR EN MARCHE NORMALE

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Abstract—The authors have determined the amount of argon-41 ejected by the stack of the EL2 reactor and the corresponding amount of γ-radiation received at ground level in the neighbourhood of Saclay, due to the argon-41. The methods used are described.

The concentration of argon-41 in the air of the stack is proportional to the reactor power and the amount is about 3×10^{-4} c/m³ for 2 MW. Since the air flow is 5·5 m³/sec, the stack emits $1{\cdot}7 \times 10^{-3}$ c of argon-41 per second when the reactor is running at 2 MW.

The greatest γ-activities at ground level outside the Centre due to argon-41 have been measured during a period of temperature inversion; they correspond roughly to 80 μr/hr.

Résumé—On a déterminé les quantités d'argon 41 rejetées par la cheminée du réacteur EL2 et les augmentations du rayonnement γ reçu au niveau du sol aux environs de Saclay dues à cet argon 41. Les méthodes utilisées sont décrites.

La concentration de l'argon 41 dans l'air de la cheminée est proportionnelle à la puissance du réacteur et atteint $3 \cdot 10^{-4}$ c/m³ à 2 MW. Le débit d'air étant de 20.000 m³/h soit 5,55 m³/s, la cheminée rejette $1{,}7 \cdot 10^{-3}$ c d'argon 41 par seconde lorsque le réacteur fonctionne à 2 MW. Les activités γ au sol, les plus fortes, dues à l'argon 41 à l'extérieur du Centre, ont été mesurées en période d'inversion de température et correspondent à environ 80 μr/h.

VOL.
1
58/9

INTRODUCTION

LES réacteurs nucléaires, ou tout au moins ceux qui sont refroidis par l'air, sont devenus une cause permanente de pollution de l'atmosphère.

En effet, l'air s'active sous l'action des neutrons du réacteur et contient ainsi, lorsqu'il est rejeté, des produits radioactifs très divers, tels que des poussières activées, de l'azote 16, de l'oxygène 19, du néon 23, du carbone 14 et de l'argon 41.

En principe, dans un réacteur bien construit, l'air est filtré avant de passer dans le réacteur et les traces de poussière qu'il rejette sont alors, en marche normale, d'activité insignifiante.

L'oxygène 19 et le néon 23 ont des périodes respectives de 29,4 s et 40 s, donc relativement très courtes, et de plus leur activité spécifique est très faible (quelques centaines de désintégrations par seconde par litre d'air dans un réacteur où l'air séjournerait dans un flux moyen de 10^{12} neutrons thermiques/cm² s); l'azote 16 a une activité spécifique importante dans le cas où il y a beaucoup de neutrons rapides (300.000 désintégrations par seconde et par litre dans un flux de 10^{12} n rapides/s cm²) mais il a une activité négligeable dans un flux de neutrons thermiques, de plus il a une période trés courte : 7,3 s.

L'activité due au carbone 14 est extrêmement faible : 0,4 désintégration par seconde et par litre. L'argon 41 a une période de 1,82 heure et donne une activité spécifique de 10.000 désintégrations par seconde et par litre pour un flux de 10^{12} neutrons thermiques/cm² s.

Le réacteur EL2 utilise, comme combustible nucléaire l'uranium naturel, comme modérateur l'eau lourde et comme réflecteur le graphite; le coeur du réacteur est refroidi par un circuit fermé de CO_2 sous pression (le CO_2 emporte ainsi la majeure partie de la chaleur dégagée dans le réacteur). Par ailleurs de l'air filtré passe sur l'extérieur de la cuve à eau lourde et sur le réflecteur de graphite, emporte ainsi quelques kilowatts supplémentaires et est rejeté par la cheminée haute de 30 mètres au débit de 5,5 m^3/s. A l'extérieur de la cuve à eau lourde il y a relativement peu de neutrons rapides, et l'activité principale est produite par l'activation de l'argon 40 par les neutrons thermiques: $^{40}A + n_{th} \rightarrow {}^{41}A + \gamma$.

Argon 40 a une section efficace de capture pour les neutrons thermiques de 0,6 barns environ.

Argon 41 émet un rayonnement comportant essentiellement un spectre β d'énergie maximum 1,24 MeV et un photon γ ayant une énergie de 1,37 MeV.

Dans ce qui suit nous utiliserons le rayonnement β pour mesurer la concentration de l'argon 41 à la sortie du réacteur et le rayonnement γ pour mesurer l'irradiation produite sur le sol qui se trouve sous le panache.

Nous indiquons ci-dessous les moyens mis en oeuvre :

(1) pour mesurer le rejet de l'argon 41 dans la cheminée du réacteur EL2
(2) pour mesurer, au sol, jusqu'à plusieurs kilomètres du réacteur, l'intensité du rayonnement γ issu du panache de ce réacteur.

Les mêmes méthodes sont applicables à d'autres réacteurs d'où s'échappe un gaz activé, en particulier à de grands réacteurs industriels comme le réacteur G1.

1. ACTIVITE DE L'ARGON 41 REJETE PAR LA CHEMINEE DU REACTEUR EL2

Appareillage

Par une dérivation faite sur la conduite qui va du réacteur à la cheminée, l'air activé par le flux de neutrons passe dans une petite chambre cylindrique dans laquelle on a placé un compteur de Geiger type 10 B 12 (compteur cylindrique à paroi mince d'aluminium 27 mg/cm^2; diamètre 20 mm, longueur utile 83 mm).

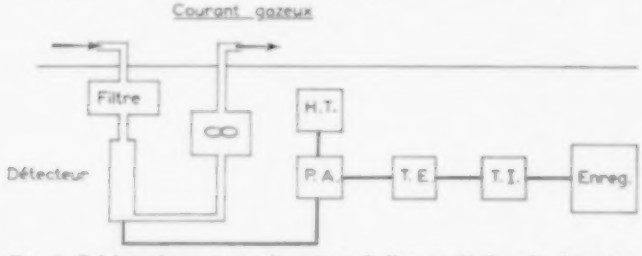

FIG. 1. Schéma du montage de mesure de l'argon 41 dans la cheminée.
HT = haute tension ; PA = préamplificateur ; TE = tiroir d'entrée ; TI = intégrateur échelle.

Les rayons β émis par l'argon 41 contenu à chaque instant dans le volume de la chambre donnent sur l'anode du compteur des impulsions qui, par l'intermédiaire d'un préamplificateur standard, sont envoyées à un tiroir d'entrée puis à un intégrateur-échelle. Le courant d'intégration, proportionnel au nombre d'impulsions par seconde alimente un enregistreur (Fig. 1).

La chambre cylindrique est précédée d'un filtre destiné à arrêter toutes les poussières qui pourraient perturber les mesures.

Le débit d'air dans la cheminée de EL2 est de 20.000 m³/h soit 5,55 m³/sec et le volume utile de la chambre cylindrique est de 286 cm³.

Mesures

Plusieurs activités ont été mesurées, notamment pour différentes puissances du réacteur. Elles sont données dans le Tableau 1. L'activité varie en pratique linéairement avec la puissance (Fig. 2). Les fluctuations sont principalement dues aux variations du bruit de fond ambiant.

TABLEAU 1. RELATION ACTIVITÉ-PUISSANCE, DANS L'AIR DE LA CHEMINÉE

Puissance (MW)	Activité (chocs/sec)		
	3 mai	23 mai	5 juin
0	2,5	5	0,5
0,10			7
0,20		22	
0,23			16
0,30		25	
0,40		35	
0,50			32
0,75			55
0,80	65	75*	
1,0		80*	68
1,1		105*	
1,2	85	80	
1,3			88
1,4	95		97
1,8	120	125	
2,0			150*

* Bruit de fond anormalement élevé.

Ainsi qu'on peut s'en rendre compte expérimentalement en fermant la chambre et en mesurant la période de décroissance, cette activité est due essentiellement à l'argon 41. L'azote 16 est très peu abondant car il n'y a pas de neutrons rapides là où passe l'air du réacteur EL2.

Etalonnage

Pour étalonner l'ensemble de mesure nous avons reproduit les conditions des expériences en utilisant de l'argon 41 d'activité bien définie. Cet argon 41 a été obtenu à partir d'un volume de 16 cm³ de l'argon 40 spectrographiquement pur que l'on a irradié dans le réacteur. Pour mesurer le flux d'irradiation on a placé dans la même ampoule que l'argon une pastille étalon de 1 cm² de manganèse. Le tout a été irradié pendant 108 minutes dans un des canaux de la colonne diffusante. La mesure, à l'aide d'un ensemble de comptage étalonné, de l'activité du manganèse, nous a permis d'évaluer le flux de neutrons à :

$$6{,}2 \cdot 10^7 \text{ neutrons thermiques/cm}^2 \text{ sec.}$$

et nous avons ainsi pu calculer l'activité prise par l'argon 40 dans le réacteur.

VOL. 1 58/9

En effet si :

$n = 6{,}02 \cdot 10^{23} \dfrac{16}{22.400}$ est le nombre d'atomes de l'argon 40 dans 16 cm³.

$\sigma = 0{,}6 \cdot 10^{-24}$ cm² est la section efficace d'activation de l'argon 40 pour les neutrons thermiques.

$\phi = 6{,}2 \cdot 10^{7}$ cm^{-2} sec^{-1} est le flux de neutrons thermiques.

$\lambda = 10{,}45 \cdot 10^{-5}$ sec^{-1} est la constante radio-active de l'argon 41.

$t = 6480$ sec est la durée d'irradiation.

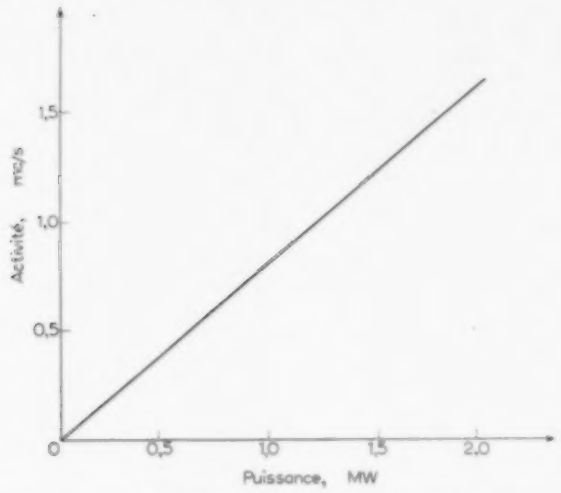

FIG. 2. Relation : activité de l'air de la cheminée, puissance thermique de EL2.

Nous avons un nombre de désintégrations β par seconde au bout d'une durée t d'irradiation :

$$N \text{ des/sec} = n\phi\sigma(1 - e^{-\lambda t})$$
$$N = 7{,}8 \cdot 10^{3} \text{ des/sec.}$$

L'argon est introduit, après le défournement dans la chambre utilisée pour les mesures. Le taux de comptage ramené à l'instant du défournement est de : 345 c/s. On en déduit le rendement de l'ensemble de mesures :

$$\frac{345}{7800} \times 100 = 4{,}4\%$$

Activité en millicuries par seconde, rejetée par la cheminée

La pollution créée dans l'air extérieur par le réacteur en fonctionnement normal a été calculée à partir des résultats de mesure dans la cheminée et de l'étalonnage de l'ensemble de mesure. Nous avons :

N nombre de chocs par seconde

$Rc = 0{,}04$ Rendement de comptage

$3{,}7 \cdot 10^{10}$ des/sec par curie

$1{,}94 \cdot 10^{4}$ = Volume rejeté par seconde/Volume utile de la chambre

et l'activité en millicuries rejetée par seconde est:

$$A = \frac{1000\ N}{3{,}7 \cdot 10^{10}\ Rc}\ 1{,}94 \cdot 10^{4}$$

$$\underline{A = 1{,}22 \cdot 10^{-2}\ N\ \text{mc/s}}$$

L'activité rejetée en fonction de la puissance du réacteur est donnée dans le Tableau 2 et représentée par la droite

$$A = kP$$

si P est exprimée en Mégawatts
et A en millicuries/seconde

$$\underline{A = 0{,}83\ P}$$

TABLEAU 2. ACTIVITÉ DUE À L'ARGON 41, REJETÉE PAR LA CHEMINÉE DE EL2 EN FONCTION DE LA PUISSANCE THERMIQUE

Puissance (MW)	Activité (mc/sec)		
	3 mai	23 mai	5 juin
0,10			0,08
0,20		0,21	
0,23			0,19
0,30		0,24	
0,40		0,36	
0,50			0,38
0,75			0,66
0,80	0,76	0,85*	
1,0		0,91*	0,82
1,1		1,22*	
1,2	1	0,91	
1,3			1,07
1,4	1,13		1,18
1,8	1,43	1,46	
2,0			1,82*

* Mesure avec bruit de fond anormalement élevé.

La cheminée du réacteur EL2 a son sommet à 30 m d'altitude au dessus d'une vaste plaine horizontale (Plateau de Saclay) et l'activité rejetée se dilue en général très vite dans l'atmosphère.

Les calculs dérivant de la loi de Sutton pour les régimes de turbulence atmosphérique, ou de considérations purement géométriques pour les régimes de subsidience dus aux inversions de température, montrent que la dose maximum permise pour les populations ($5 \cdot 10^{-8}$ c/m^3) n'est jamais atteinte en un point quelconque du terrain situé autour du réacteur, lorsque celui-ci rejette les activités indiquées dans le Tableau 2.

De même les calculs ont montré que l'intensité du rayonnement γ dû au panache, ne dépassait jamais en un point quelconque du sol la dose maximum permise pour les populations (180 μr/h), dans les conditions ci-dessus.

VOL. 1 58/9

Cependant afin de s'assurer de l'exactitude de ces dernières prévisions, des mesures au sol ont été faites, qui sont décrites ci-après.

2. ACTIVITE γ AU SOL, DUE AU PANACHE DU REACTEUR EL2

Les mesures sous le panache du réacteur EL2 ont été faites uniquement dans le but de mesurer le rayonnement γ reçu au sol et nous n'avons pas jugé bon jusqu'ici, de déterminer les concentrations de l'argon 41 dans l'air. En effet la faiblesse des valeurs trouvées pour le rayonnement γ indique qu'on ne peut avoir au sol une pollution supérieure à la dose maximum permise (population). La forme du panache, sa hauteur, ses dimensions dépendent, d'une part de la vitesse et de la température de sortie des gaz, de la hauteur de la cheminée, d'autre part des conditions météorologiques locales: gradient de température, turbulence, vitesse de vent. Les premiers paramètres sont connus et constants:

θ 10° au dessus de la température ambiante
$h = 30$ m
$v = 7$ m/s

et ont été utilisés pour les calculs de la pollution et de l'irradiation au sol. L'influence des paramètres météorologiques à basse altitude est difficile à déterminer et ceci nous a amené à faire les mesures de l'irradiation au sol pour des conditions météorologiques différentes.

Appareillage

Les mesures du rayonnement γ dû à l'argon 41 ont été faites à l'aide d'un ensemble à scintillations.* Un photo-multiplicateur EMI 6099 porte sur sa photocathode de 100 cm² trois cristaux de NaI (Tl) HARSHAW ($1\frac{3}{4}$ in. $\times$ 2 in.). Les rayons γ qui

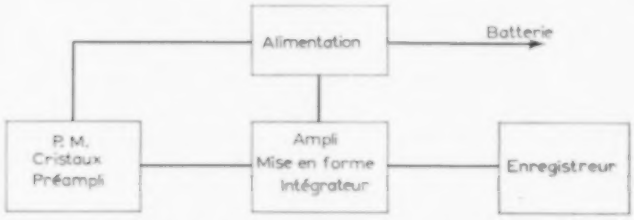

FIG. 3. Schéma du scintillomètre SP3.

traversent les cristaux produisent des impulsions limineuses qui sont transformées en impulsions de tension par la photocathode du photomultiplicateur. Après amplification par le photomultiplicateur les impulsions de tension sont mises en forme et intégrées. Le courant d'intégration est envoyé à un enregistreur à avance mécanique. La déviation totale de cet appareil est obtenue pour 1.000 impulsions produites par seconde par le photomultiplicateur (Figs. 3 et 4). L'ensemble de l'appareillage est monté sur une voiture tous terrains dont on utilise la batterie comme source d'énergie.

* Scintillomètre SP3–MESCO.

VOL.
1
58/9

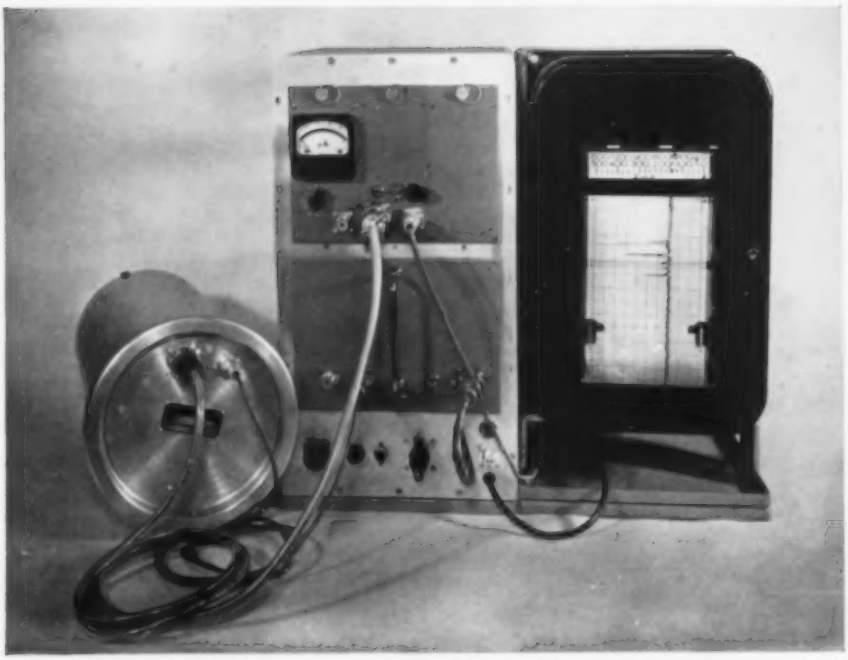

FIG. 4. Ensemble à scintillations SP3.
A gauche : détecteur.
Au milieu { en bas—alimentation
en haut—intégrateur et contrôle
A droite : enregistreur.

VOL
1
1958/

Etalonnage

Pour étalonner l'ensemble SP3 en unités d'irradiation (roentgen) nous avons utilisé une source de cobalt 60 dont les rayons γ ont une énergie voisine de celle des rayons γ de l'argon 41

$$^{60}\text{Co} \quad \gamma \begin{cases} 1{,}17 \\ 1{,}33 \end{cases} \text{MeV}$$

$$^{41}\text{A} \quad \gamma \quad 1{,}37 \text{ MeV}$$

Les deux rayons γ du cobalt 60 sont émis lors de chaque désintégration. Une source de 315 μc de cobalt 60 placée à 2m.50 au dessus des cristaux de NaI provoque une augmentation du taux de comptage de 620 chocs/sec.

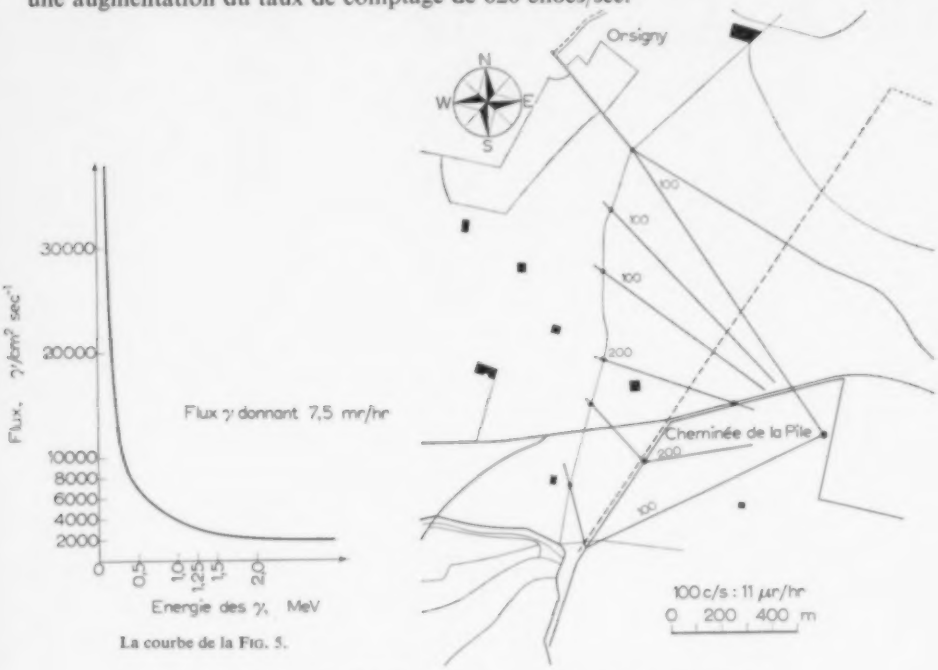

FIG. 5. Rayonnement γ au sol (en chocs/sec) sous le panache d'EL2 par vent d'est (10,2 m/s). Puissance du réacteur 1,7 MW.

Pour calculer l'irradiation produite par cette source à l'endroit où est placé le détecteur, prenons comme valeur moyenne de l'énergie des rayons γ du cobalt 60 1,25 MeV. Il nous faut convertir le nombre de microcuries de la source en microroentgen. L'unité curie correspond à $3{,}7 \cdot 10^{10}$ désintégrations par seconde. Le roentgen correspond à l'absorption d'une énergie de 83,8 ergs par gramme d'air. Pour relier l'unité curie à l'unité roentgen dans le cas du cobalt 60 nous utilisons la courbe de la Fig. 5. Cette courbe extraite d'un déclassé par DUNSTER* donne pour chaque énergie des γ le flux de ces rayons γ nécessaire pour produire une irradiation de 7,5 mr/h. Nous lisons sur cette courbe que pour l'énergie de 1,25 MeV du cobalt 60 il faut 3200 γ/cm² sec pour produire 7,5 mr/h.

* H. J. DUNSTER. *An Anthology of Health Physics Data* (2nd Ed.). Research and Development Branch, Windscale, Tech. note no. 58 (Oct. 1954).

Notre source de 315 μc donne à 2m.50 un flux égal à :

$$\frac{315 \cdot 10^{-6} \cdot 2 \times 3{,}7 \cdot 10^{10}}{4\pi\ 250^2}\ \gamma/\text{cm}^2\ \text{sec.}$$

En tenant compte des éléments suivants :

2 rayons γ par désintégration
$3{,}7 \cdot 10^{10}$ désintégrations par seconde pour 1 curie
$4\pi\ 250^2$ surface de la sphère de rayon 250 cm
$\phi = 29{,}6\ \gamma/\text{sec cm}^2$.

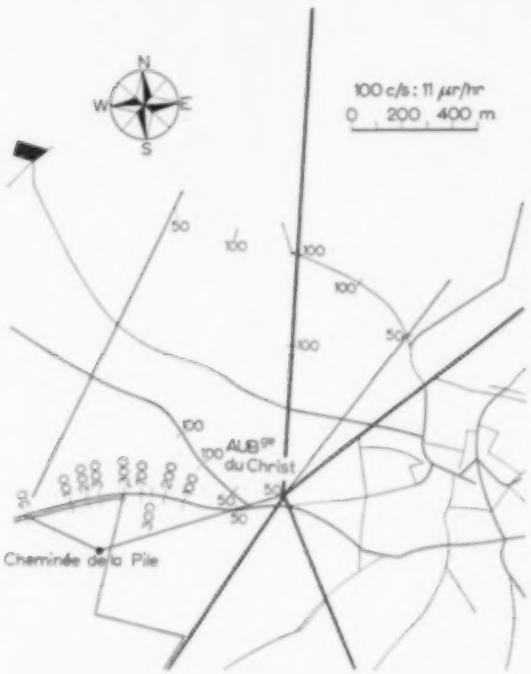

FIG. 6. Rayonnement γ au sol (en chocs/sec) sous le panache d'EL2 par vent d'ouest-sud-ouest (4 m/s). Puissance du réacteur 1,7 MW.

D'où l'irradiation en roentgen/heure

$$\frac{29{,}6}{3.200}\ 7{,}5 \cdot 10^{-3} = 69{,}5 \cdot 10^{-6}\ \text{r/h}$$

620 chocs/sec correspondent à 69,5 μr/h

100 chocs/sec correspondent à $\frac{69{,}5}{620} \times 100 = 11{,}2\ \mu\text{r/h}$.

$$\underline{100\ \text{c/s} : 11{,}2\ \mu\text{r/h}.}$$

Les doses maxima permises sont:

Pour les populations: 30 mr/semaine (168 h) soit 180 μr/h
Pour le travail: 300 mr/semaine (40 h) soit 7,5 mr/h

A l'extérieur du centre, nous devons prendre pour dose maximum permise:

180 μr/h

100 c/s sont équivalents à $11,2 \cdot 10^3/180 = 62$ millidoses population.

100 c/s: 62 mdoses population

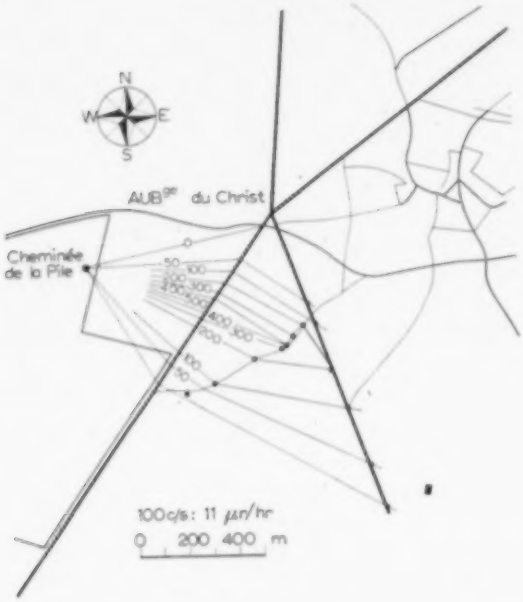

FIG. 7. Rayonnement γ au sol (en chocs/sec) sous le panache d'EL2 par vent de nord-ouest (1 m/s). Puissance du réacteur 1,7 MW.

Mesures

Une série de mesures a été faite du 21 avril au 5 mai 1957, sous différente conditions météorologiques.

Chaque mesure se traduit sur la carte de la région par un ensemble de points d'activité déterminée. Chaque fois que celà a été possible, nous avons joint les points de même activité pour donner une allure générale du panache. Par vent fort ces points de même activité sont très dispersés et nous nous sommes alors contentés de les inscrire avec leur valeur.

En deux semaines nous avons eu à peu près toutes les directions de vent, donc de panache, ainsi que des conditions de pollution très différentes. Nous joignons à ce rapport quatre des tracés obtenus au cours de ces mesures, chaque tracé correspond à une direction et à une vitesse de vent. Les conditions les plus critiques ont été rencontrées lors des inversions de température (5 mai). Dans ces conditions le

VOL. 1 58/9

panache se dilue et se disperse très peu; l'activité reste sensible à des distances supérieures à 4 km.

Ces mesures nous ont permis de vérifier que les doses maxima permises ne sont jamais atteintes en fonctionnement normal, puisque nous aurions mesuré un maximum de 0,6 dose si le réacteur avait eu la puissance thermique maximum prévue de

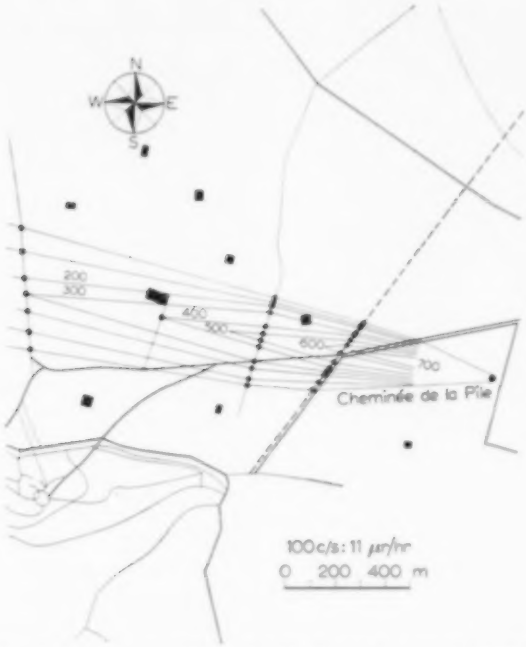

FIG. 8. Rayonnement γ au sol (en chocs/sec) sous le panache d'EL2 par vent d'est-est-sud (<1 m/s) et inversion de température. Puissance du réacteur 1,7 MW.

2 MW. Sur le Plateau de Saclay il n'y a pas de vent dominant, donc pas de direction privilégiée pour le panache et les inversions de température lorsqu'elles se produisent ne durent que quelques heures par jour. Au total l'irradiation produite en un point au cours d'une année reste très inférieure à la limite maximum admise et ne crée aucun danger pour les populations.

CONCLUSION

Les mesures effectuées tant à l'intérieur de la cheminée du réacteur EL2 qu'à l'extérieur du Centre sous le panache de ce réacteur nous ont permis de vérifier que l'activité rejetée en fonctionnement normal ne constitue aucun danger pour les populations avoisinant le Centre. De plus ces mesures ont prouvé que les méthodes et appareillages utilisés sont suffisamment sensibles et précis pour être utilisés dans tous les cas de vérifications de pollution ou d'irradiation par la cheminée d'un réacteur.

VOL
1
1958/

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THE COLORIMETRIC DETERMINATION OF SULFUR OXIDES IN ATMOSPHERE

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(*Received* 15 *August* 1958)

Abstract—In this report are described first the colorimetric determination of the total sulfur oxides in atmosphere, and second, the colorimetric modification of the lead peroxide method. The determination of the sulfur oxides can be carried out exactly and concisely by these colorimetric methods.

(A). THE COLORIMETRIC DETERMINATION OF THE TOTAL SULFUR OXIDES IN ATMOSPHERE

IN air pollution studies on the presence of sulfur oxides it is necessary to determine both SO_2 and SO_3 at the same time and place, for both sulfur oxides are present simultaneously. For this purpose the method of BERTOLACINI and BARNEY (1956) has been adapted for atmospheric sampling. This colorimetric method makes use of barium chloranilate for the determination of sulfate.

The method is based on the reaction of solid barium chloranilate with sulfate ion at pH 4 in 50 per cent ethyl alcohol solution to liberate highly colored acid-chloranilate ion. For the estimation of the concentration the broad absorption peak at 530 μ is used.

The sulfate solution is obtained by passing polluted air through a $\frac{1}{2}$ per cent aqueous solution of hydrogen peroxide. BERTOLACINI and BARNEY used solutions containing 20–200 γ sulfate/ml as potassium sulfate and recorded a standard deviation and relative error of the method for the standards of 1 per cent. At atmospheric concentrations of 0·05 p.p.m. of sulfur oxides a sampling time of 24 hr at a rate of 3–5 l/min was adopted to attain similar accuracy.

The concentration of SO_3 originally present is obtained by subtracting the value of SO_2 from that of the total sulfur oxides.

Reagents

(1) Barium chloride, reagent grade.
(2) Chloranilic acid (2,5-dichloro-3, 6-dihydroxy-*p*-quinone). Eastman, practical grade.
(3) Barium chloranilate. Barium chloranilate is prepared by mixing 1 l. of 0·1 per cent aqueous chloranilic acid with 1 l. of 5 per cent aqueous barium chloride and permitting the mixture to stand overnight at room temperature. The aged precipitate is washed with water until the supernatant liquid is free of chloride ion. Water is removed by centrifuging the precipitate three times with ethyl alcohol and once with diethyl ether and drying it for 1 hr at 60° C in a vacuum oven.
(4) Buffer, pH 4·0: 0·05 M solution of reagent grade potassium acid phthalate.
(5) Absorbent solution: 0·1 per cent aqueous solution of H_2O_2.
(6) Standard solution: 634 mg of anhydrous sodium sulfate are dissolved in water and diluted to 1 l. 1 cm³ of the standard solution = 0·1 cm³ of gas (standard condition).

Procedure

100 cm³ of the absorbent solution are taken in a tube and air is passed through the solution at a rate of 3–5 l/min for 24 hr. After the absorption has finished, the solution is taken in a beaker and the volume concentrated to v cm³ (usually 25 cm³) on the water bath. To each 5 cm³ of this concentrated solution and standard solution are added 5 cm³ of the buffer solution, 10 cm³ of 95 per cent ethyl alcohol and 0·1 g of barium chloranilate. The mixture is shaken for 10 min. The excess barium chloranilate and the precipitated barium sulfate are removed by filtering. The absorbance of each of the filtrates (E and E_0) is measured with a colorimeter at 530 mμ vs. a blank prepared in the same manner. The concentration of sulfur oxides is calculated according to the following formula:

$$0{\cdot}1 \times \frac{E}{E_0} \times \frac{v}{V} \times 1000 = \frac{100Ev}{E_0V} \text{ p.p.m.}$$

Here, V is the total passing air volume (l.).

Discussion

The absorption efficiency of sulfur oxides by the absorbent solution is nearly 100 per cent. The residual presence of H_2O_2 and CO_2 did not interfere with the colorimetric method. The minimum concentration of sulfur oxides measured by this method is about 0·05 p.p.m. If the concentration would be lower than 0·05 p.p.m., the volume of v mentioned above should be under 25 cm³.

(B) THE COLORIMETRIC MODIFICATION OF THE LEAD PEROXIDE METHOD FOR MEASURING SULFUR OXIDES IN ATMOSPHERE

The lead peroxide method, which is useful for measuring the extent of atmospheric pollution by sulfur oxides, has been hitherto gravimetric. If this method would be converted to colorimetry, the procedure may be more easily simplified and the test period, during which the lead cylinder is exposed in atmosphere, may be shortened. In this section, the colorimetric modification by the use of barium chloranilate reagent is described. By the practical application of this method, it is possible that 10 days are enough as the test period, even when the concentration of sulfur oxides is 1 mg SO_3 per day per 100 cm² of PbO_2.

Reagents

(1) Sodium carbonate solution: 4 per cent aqueous solution.
(2) 5 per cent hydrochloric acid solution: previously, 20 cm³ of sodium carbonate solution are titrated with 5 per cent hydrochloric acid in the presence of methyl red solution as an indicator (v cm³).
(3) Barium chloranilate: mentioned above.
(4) Buffer solution: mentioned above.
(5) Standard solution: mentioned above.

Procedure

After the test period has elapsed for 10 days, the lead cylinder is removed from the apparatus. The fabric coated with 4 g of lead peroxide is stripped off, added in 50 cm³ of 4 per cent sodium carbonate solution and warmed on the water bath for 1 hr,

VOL 1 1958/

then diluted to 100 cm³ with water, and filtered from the lead peroxide. 40 cm³ of the filtrate are then taken, and v cm³ of 5 per cent hydrochloric acid solution added for neutralization. The solution is then diluted exactly to 50 cm³ with water. To each 5 cm³ of this solution and standard solution are added 5 cm³ of the buffer solution, 10 cm³ of 95 per cent ethyl alcohol and 0·1 g of barium chloranilate. The mixture is shaken for 10 min. The excess barium chloranilate and the precipitated barium sulfate are removed by filtering. The absorbance of each of the filtrates (E and E_0) is measured with a colorimeter at 530 mμ vs. a blank prepared in the same manner. The results of observations are reported as mg SO_3 per day per 100 cm² of PbO_2 according to the following formula:

$$0{\cdot}634 \times \frac{SO_3}{Na_2SO_4} \times \frac{E}{E_0} \times \frac{50}{40} \times \frac{100}{n} = \frac{44{\cdot}6 \times E}{n \times E_0}$$

Here, n is the number of days of the test period.

Discussion

The presence of lead peroxide and the neutralization of sodium carbonate with hydrochloric acid did not affect the results. The sensitivity of the method was satisfactory, since the extinction (E) was distinctly discernible even in the case of 1 mg of SO_3 per day per 100 cm² of PbO_2.

CONCLUSION

Barium chloranilate was applied to the determination of sulfur oxides in air. The hydrogen peroxide method for determining the total sulfur oxides and the lead peroxide method for measuring the extent of atmospheric pollution by sulfur oxides were simplified. The latter especially is convenient for the detailed observations of air pollution by sulfur oxides, as the test period can be shortened to 10 days.

Acknowledgements—The author is deeply grateful to Prof. T. UKITA of the University of Tokyo for his kind advice and encouragement.

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VOL. 1 58/9

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ATMOSPHERIC SO_2 CONCENTRATIONS OBSERVED IN KEIHIN INDUSTRIAL CENTER AND THEIR RELATION TO METEOROLOGICAL ELEMENTS

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(*Received* 15 *August* 1958)

Abstract—Atmospheric sulfur dioxide concentrations have been measured in one of the most important industrial areas of Japan, the Keihin manufacturing district between Tokyo and Yokohama. The SO_2 concentrations measured over a 1-yr period did not exceed 0·19 parts per million. The data were correlated with daily, seasonal, climatological and meteorological data.

DURING a 1-yr period from February, 1957, to February, 1958, the authors performed a series of analyses on the concentration of atmospheric sulfur dioxide in the Keihin manufacturing district, one of the most important industrial centers of Japan (Fig. 1). For the determination of the atmospheric SO_2 the method reported by WEST and GAEKE (1956) was used. The data obtained have been related to daily, seasonal and meteorological factors. The monthly variation of the concentration of SO_2 with respect to time of day is shown in Fig. 2, and the seasonal variation in Fig. 3.

Diurnal variation of frequency (per cent) of occurrence of SO_2 concentration at greater than 0·03, 0·06 and 0·10 p.p.m. levels are shown in Table 1 and Fig. 4. The annual variations are shown in Table 2 and Fig. 5, and the annual variation in

TABLE 1. DIURNAL VARIATION OF FREQUENCY (%) OF OCCURRENCE OF CLASSIFIED SO_2 CONCENTRATION IN EACH SEASON

Season	Hour / SO_2 concn. (ppm.)	0–2	2–4	4–6	6–8	8–10	10–12	12–14	14–16	16–18	18–20	20–22	22–24
Winter	>0·03	49·9	36·4	77·7	73·2	73·2	62·1	74·5	65·9	66·8	83·2	80·0	60·1
	>0·06	24·9	9·1	11·1	20·0	40·9	25·3	30·9	40·3	25·1	56·0	33·5	13·3
	>0·10	0	0	0	0	0	0	12·9	22·9	8·4	16·8	13·4	0
Spring	>0·03	0	0	0	4·7	85·7	27·5	26·7	20·4	20·6	23·5	12·5	9·5
	>0·06	0	0	0	0	42·7	13·7	5·0	11·1	8·8	8·8	0	0
	>0·10	0	0	0	0	21·4	3·4	3·3	1·9	0	0	0	0
Summer	>0·03	0	0	0	10·0	7·7	0	13·7	11·7	6·4	0	0	0
	>0·06	0	0	0	0	0	0	0	0	0	0	0	0
	>0·10	0	0	0	0	0	0	0	0	0	0	0	0
Autumn	>0·03	0	0	0	0	21·4	9·6	15·3	0	0	41·6	0	0
	>0·06	0	0	0	0	0	0	0	0	0	0	0	0
	>0·10	0	0	0	0	0	0	0	0	0	0	0	0

FIG. 1. Location of SO_2 observation station.

VOL. 1 58/9

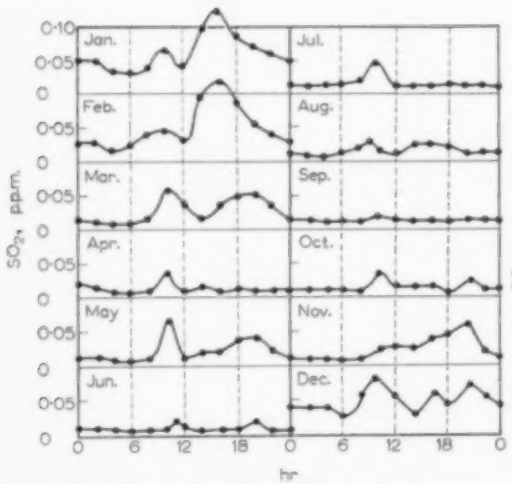

FIG. 2. Diurnal variation of SO_2 concentration vs. month of year.

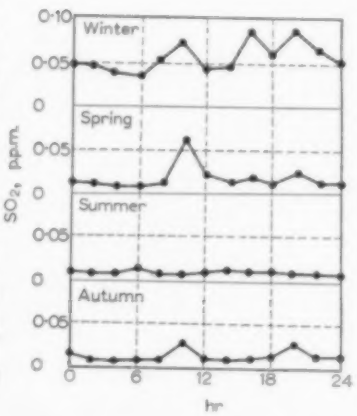

FIG. 3. Diurnal variation of SO_2 concentration vs. season of year.

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TABLE 2. ANNUAL VARIATION OF SO_2 CONCENTRATION

Month	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
No. of observations (ppm)	125	117	125	338	117	150	64	119	69	149	61	149
Max. concn. of SO_2 (ppm)	0·190	0·173	0·109	0·189	0·114	0·044	0·089	0·056	0·017	0·050	0·071	0·134
Min. concn. of SO_2 (ppm)	0·007	0	0	0	0	0	0	0	0·003	0·002	0	0·011
Average concn. of SO_2 (ppm)	0·054	0·060	0·023	0·015	0·023	0·010	0·012	0·010	0·007	0·020	0·018	0·046

TABLE 3. RELATION BETWEEN SO_2 CONCENTRATION AND WEATHER CONDITIONS

Weather	No. of observations	Average concn. of SO_2 (ppm)	Average wind velocity (m/sec)
Clear	424	0·027	5·3
Cloudy	383	0·024	4·9
Rainy	205	0·013	5·1

frequency (per cent) of occurrence of SO_2 concentration greater than 0·03, 0·06 and 0·10 p.p.m. are presented in Fig. 6.

Rainy periods, especially those from March to June, afforded an opportunity to study the action of rain on the removal of SO_2 from the air. Table 3 and Fig. 7 show that during rainy periods the SO_2 concentrations are lower. Of interest is the rapid drop in SO_2 concentration presented in Fig. 7, where the scrubbing action of the rain

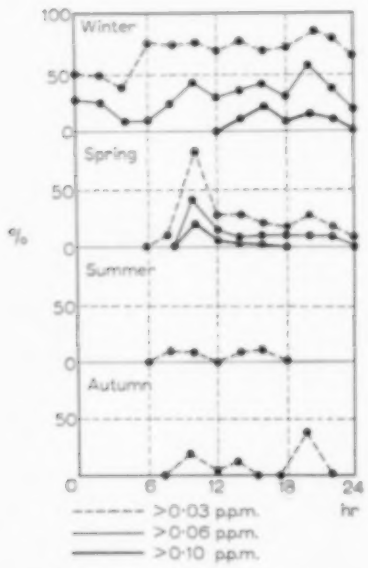

FIG. 4. Diurnal variation of frequency (%) of occurrence of classified SO_2 concentrations in each season.

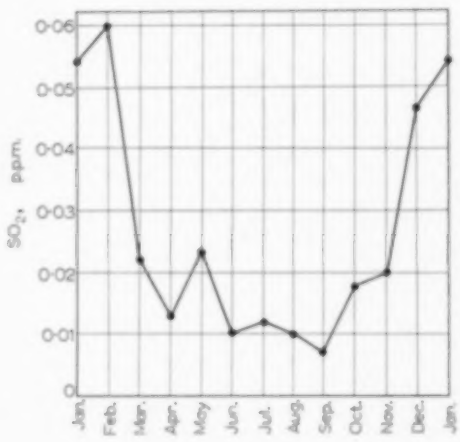

FIG. 5. Annual variation in SO_2 concentration.

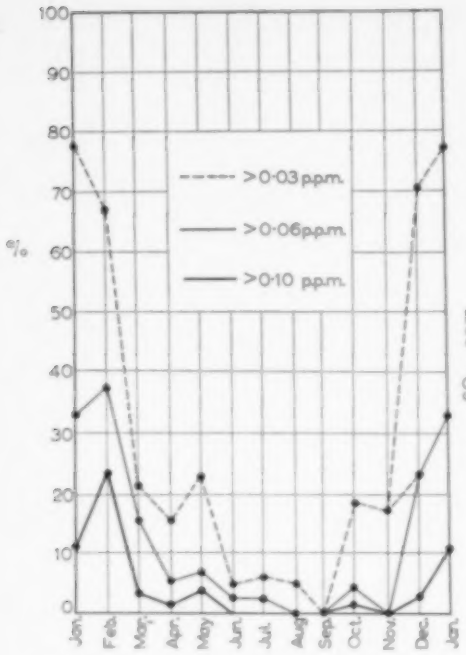

FIG. 6. Annual variation of frequency (%) of occurrence of classified SO_2 concentrations.

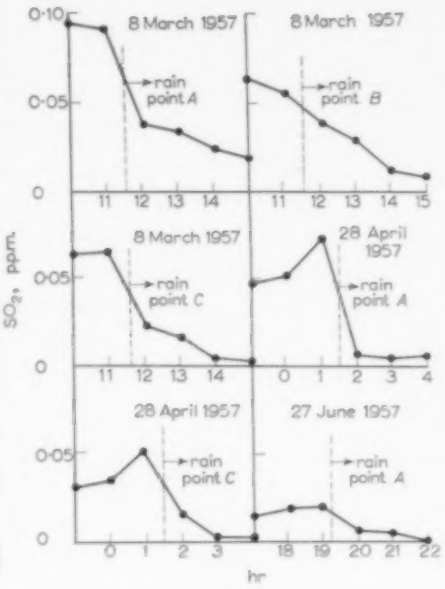

FIG. 7. Influence of rain on SO_2 concentration.

removes most of the pollutant in a few hours. As a consequence the hourly variation of SO_2 concentration under rainy conditions is less than for clear weather (Fig. 8).

The relation between wind direction and SO_2 concentration is shown in Fig. 9 (a), (b) and (c), and between wind velocity, in Figs. 10 and 11. Hourly variation of SO_2 concentration and atmospheric temperature lapse rate are shown in Fig. 12, vertical distribution of SO_2 concentration and temperature in Fig. 13.

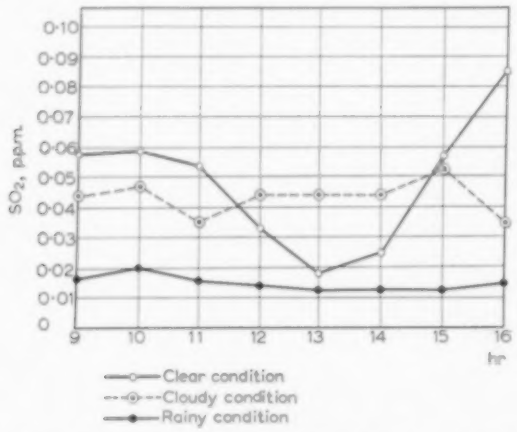

FIG. 8. Hourly variation of SO_2 concentration in each weather condition.

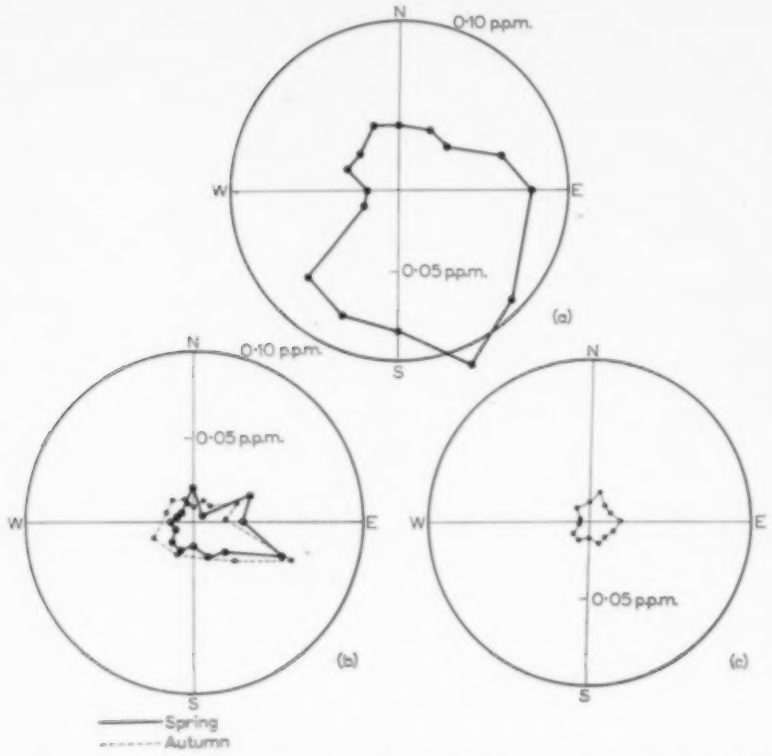

FIG. 9. Relation between SO_2 concentration and wind direction (except for rainy conditions (a) in winter (b) in spring and autumn (c) in summer.

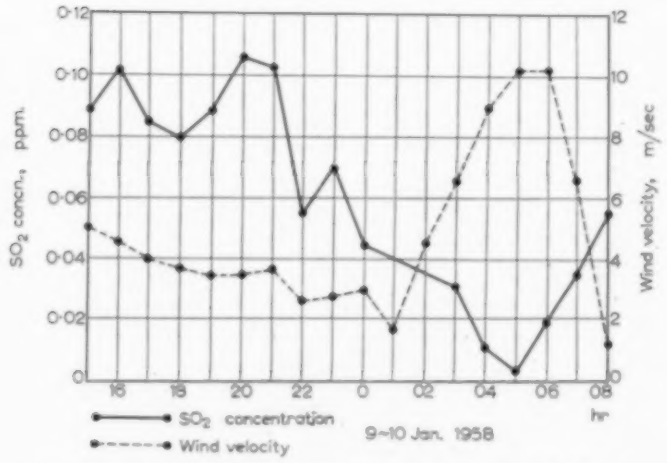

FIG. 10. Hourly variation of SO_2 concentration and wind velocity.

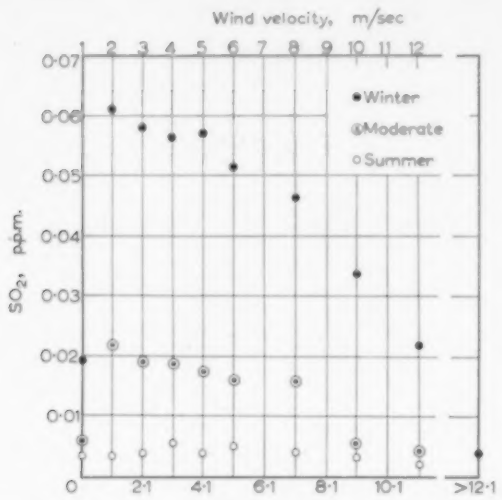

FIG. 11. Relation between SO_2 concentration and wind velocity.

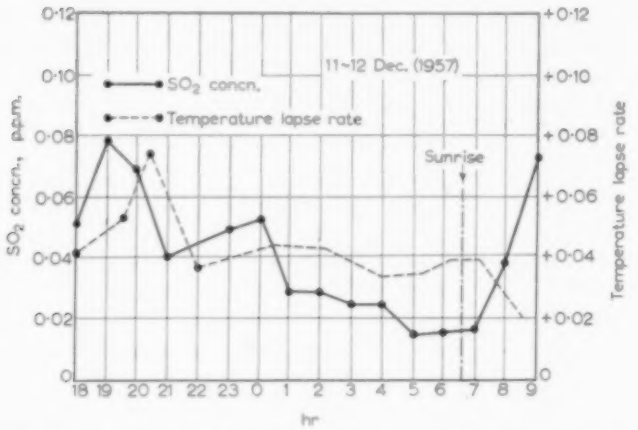

FIG. 12. Hourly variation of SO_2 concentration and atmospheric temperature lapse rate.

CONCLUSIONS

(1) The concentration of sulfur dioxide varies with the season, the order of decreasing concentration being winter > spring > autumn > summer.

(2) In February the highest concentrations were found, while December and January were markedly higher than the other nine months of the year. Concentrations found in the period of June through September were equally very low, while intermediate values were observed in March, April, May, October and November.

(3) Generally the concentration varied during the day in accordance with a standard variation curve containing two maxima, at 8.00 a.m. and 6.00–8.00 p.m. In summer

VOL. 1 58/9

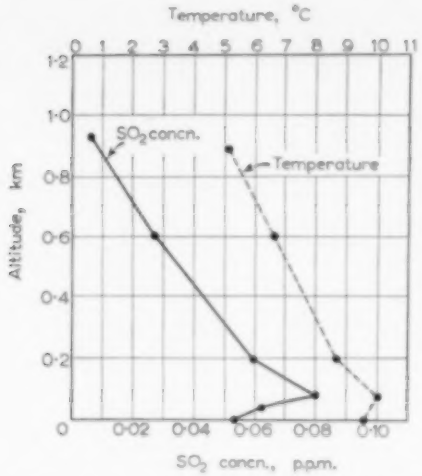

FIG. 13. Vertical distribution of SO_2 concentration and temperature.

or early autumn low concentrations were sometimes maintained throughout the day, and in winter a third maximum was observed at 4.00 p.m.

(4) The effect of wind shifts was distinctly noticeable. When it blew from a southerly or easterly direction the concentration increased, while a northerly or westerly wind resulted in decreased SO_2 concentrations.

(5) The concentration of sulfur dioxide was inversely proportional to the wind velocity, due probably to the dilution effect of greater volumes of air.

(6) Rainfall markedly diminishes the concentration of sulfur dioxide by washing it to the earth. However, on cloudy days, the contamination may be expected to remain for a long period.

(7) After sunrise, the concentration of sulfur dioxide was proportional to the degree of atmospheric stability; conversely, after sunset the maximum concentration occurred during a period when the atmosphere was becoming less stable. The vertical distribution of sulfur dioxide varied with temperature: the concentration increased through the temperature inversion and decreased above it.

(8) The concentration of sulfur dioxide was inversely proportional to the height above ground of the base of the temperature inversion layer.

Acknowledgement—The authors are deeply grateful to Prof. T. UKITA of the University of Tokyo for his kind advice and encouragement.

REFERENCE

WEST P. W. and GAEKE G. C. (1956) *Anal. Chem.* **28**, 1816–9.

Int. J. Air Poll. Pergamon Press 1959. Vol. 1, p. 241. Printed in Great Britain.

Review Articles

THE TECHNICAL PROVISIONS OF THE BRITISH CLEAN AIR ACT—REGULATIONS FOR SCOTLAND

G. NONHEBEL
Imperial Chemical Industries, Millbank, London, S.W. 1

THE industrial provisions of the Clean Air Act, 1956, came fully into operation in England and Wales on 1 June 1958 with the issue of many technical regulations (NONHEBEL, 1958). The Act allows different regulations for Scotland and these have now been issued and came into operation on 31 December 1958. The regulations for permitted periods of dark smoke from land installations and from ships are the same as for England and Wales.

Under the associated Alkali Works (Scotland) Order, the list of noxious and offensive gases and the list of works scheduled under the Scottish Alkali Works Regulations Act of 1906 have been extended so that the position in Scotland corresponds to that in England and Wales. There are slight differences in wording between the Scottish and English lists with which the general reader need not be concerned. There are also the following additions:

(*a*) The definition of Aluminium Works in Scotland has been extended to include works in which aluminium is extracted from any material containing aluminium by a process evolving any noxious or offensive gases or in which oxide of aluminium is extracted from an ore.

(*b*) The definition of Caustic Soda works has been extended to include " works in which black liquor produced in the manufacture of paper is calcined in the recovery of caustic soda ".

The new official documents concerned are:

Statutory Instrument	*Title*
1958 No. 1931 (C.11) (S.104)	Clean Air Act 1956 (Appointed Day No. 2) (Scotland) Order, 1958
1958 No. 1932 (S.105)	The Alkali etc. Works (Scotland) Order, 1958
1958 No. 1933 (S.106)	The Dark Smoke (Permitted Periods) (Scotland) Regulations, 1958
1958 No. 1934 (S.1067)	The Dark Smoke (Permitted Periods) (Vessels) (Scotland) Regulations, 1958

REFERENCE

NONHEBEL G. (1958) The technical provisions of the British Clean Air Act. *Int. J. Air Poll.* **1**, 120.

Int. J. Air Poll. Pergamon Press 1959. Vol. 1, pp. 242–48. Printed in Great Britain.

RESEARCH IN AIR POLLUTION IN THE UNITED KINGDOM

This brief description of the research in air pollution in the United Kingdom is a shortened version of a longer note (Bulletin No. 17), copies of which may be obtained from the Department of Civil Engineering, King's College, Newcastle upon Tyne.

October 1958

PETER C. G. ISAAC

A. GOVERNMENT DEPARTMENTS

A.1 Ministry of Agriculture, Fisheries & Food,
National Agricultural Advisory Service,
Great Westminster House,
Horseferry Road,
London, S.W.1.
Director: (Great House Experimental Husbandry Farm) C. H. MUDD, B.Sc.

The study, on a practical basis, of husbandry practices which might alleviate the effects of the pollution, is being carried out.

A.2 Ministry of Agriculture, Fisheries & Food,
Central Veterinary Laboratory,
New Haw,
Weybridge,
Surrey.
Director: A. W. STABLEFORTH, D.Sc., M.R.C.V.S., D.V.S.M.

Research projects concern the hazard to farm animals arising from the aerial contamination of herbage by emission of particulate and gaseous fluorides from industrial works.

A.3 Forestry Commission,
25, Savile Row,
London, W.1.
Director of Research and Education: J. MACDONALD

The growth of a variety of species is being studied in a heavily polluted atmosphere in the Pennines. Measures are being made of the deposit of SO_3.

A.4 Ministry of Fuel and Power,
Safety in Mines Research Establishment,
Portobello Street,
Sheffield, 1.
Director: H. T. RAMSEY

The amount and composition of smoke produced by burning contrasted types of coal under controlled conditions of temperature and oxygen supply are being investigated. (This work is done jointly with the Department of Fuel Technology of Sheffield University.)

Attempts are also made to develop techniques for distinguishing different components of air pollution by electron microscopy and to reproduce in the laboratory a number of effects such as droplet formation observed in air-pollution samples of town air.

A.5 Meteorological Office,
Air Ministry,
Kingsway,
London, W.C.2.
Director: Sir GRAHAM SUTTON, C.B.E., D.Sc., F.R.S.

VOL 1 1958

Atmospheric turbulence in the first few thousand feet above the ground. Atmospheric diffusion. Effect of air pollution on fog. Effect of pollution on visibility.

A.6 Chemical Defence Experimental Establishment,
Porton,
Salisbury,
Wiltshire
under the auspices of
Ministry of Supply
Director of Chemical Defence Research & Development,
Room 430,
Shell Mex House,
Strand,
London, W.C.2.

Distribution of particle and droplet size. Development and use of protective masks, especially for chronic bronchitics and asthmatics.

B. GOVERNMENT RESEARCH ORGANIZATIONS

B.1 Department of Scientific and Industrial Research,
Building Research Station,
Garston,
Watford,
Hertfordshire.
Director: Dr. F. M. Lea

VOL.
1
58/9

The B.R.S. is concerned with the durability of building materials and therefore takes an interest in the effects of air pollution on buildings stones and slates, bricks, paints and metals.

B.2 Department of Scientific and Industrial Research,
Warren Spring Laboratory,
Stevenage,
Hertfordshire.
Director: S. H. Clarke, C.B.E.

To devise methods for the recognition and determination of specific polluting agents in the concentrations at which they are present in flues and in the atmosphere. Prevention of pollution leaving furnaces or engines. Research on polluting agents in the atmosphere. Organization and evaluation of results of the D.S.I.R. Co-operative Survey of air pollution.

B.3 Medical Research Council,
38, Old Queen Street,
Westminster,
London, S.W.1.
Secretary: Sir Harold Himsworth, K.C.B., M.D., Ll.D., F.R.S.

Analysis of vehicle exhausts under experimental conditions (see E.1).

Study of the development of chronic bronchitis in animals and the subsequent effects of pollutants on them.

Studies in the prevalence of chronic bronchitis amongst G.P.O. employees in areas of contrasting pollution.

Trials of the possible value of ammonia in protection of susceptible patients from the effects of acute pollution.

Trials of the value of smog masks and experimental air conditioners.

(See also entries B.4, B.5, and E.1.)

B.4 Medical Research Council Group for Epidemiological Research on Respiratory Diseases (Air Pollution),
Department of Social and Industrial Medicine,
University of Sheffield.
Director: Professor C. H. STUART-HARRIS, M.D., F.R.C.P.
Staff: Dr. M. CLIFTON, M.D., J. K. DONOGHUE, B.Sc., D. F. KERRIDGE, B.Sc.

The aim of the Group is to investigate the epidemiology of respiratory diseases, with special reference to bronchitis and air pollution.

B.5 Medical Research Council,
Group for Research on Atmospheric Pollution,
Dunn Laboratories,
St. Bartholomew's Hospital,
London, E.C.1.
Director: Dr. P. J. LAWTHER, M.B., M.R.C.P.

The Group is concerned primarily with the investigations of the clinical aspects of community air pollution. Studies are being made on the physical and chemical characteristics of pollutants, and on the significance of polluted air in relation to lung cancer and chronic bronchitis. The Group works in close co-operation with the Government departments in Britain and in the U.S.A.

C. NATIONALIZED INDUSTRIES

C.1 Central Electricity Generating Board,
Research and Development Department, Operations Branch,
24/30 Holborn,
London, E.C.1.
Director: R. Ll. REES
Deputy Director: Dr. H. E. CROSSLEY

Surveys of atmospheric pollution around power-stations by monthly measurements. Short-term measurements of sulphur-dioxide pollution around power-stations. Studies of the behaviour of chimney plumes. The development of new testing techniques.

C.2 The Gas Council,
1, Grosvenor Place,
London, S.W.1.
Secretary: F. G. BREWER, O.B.E., M.A.

The Gas Council conducts research on a large scale into the production of gas and coke and the use of gas and coke by consumers. Research effort is directed towards more efficient methods of production and more efficient gas and coke-burning appliances.

C.3 London Transport Executive,
Research Department,
55, Broadway,
Westminster,
London, S.W.1.
Director: A. T. WILFORD, A.R.C.S., B.Sc., F.R.I.C., F.S.S., C.I.Mech.E., F.Inst.Pet.

Work is done in collaboration with the Department of the Chief Mechanical Engineer (Road Services) on the problem of exhaust-smoke emission from diesel-engined buses and coaches.

VO
1
1958

C.4 National Coal Board,
Queensborough House,
12/18 Albert Embankment,
London, S.E.11.
Director General of Research :
W. IDRIS JONES

National Coal Board,
Coal Research Establishment,
Stoke Orchard,
Cheltenham, Gloucestershire.
Director : Dr. J. BRONOWSKI

The National Coal Board is actively engaged in research on the production of solid smokeless fuels suitable for the domestic market. The supply of materially smokeless coals is limited in sizes suitable for this market, and efforts now reaching the pilot-plant scale are being made to increase the quantities available by the binderless briquetting of the very small sizes of such coals. The increases obtainable by this method are, however, limited, and other processes are being investigated.

C.5 The National Coal Board,
Hobart House,
Grosvenor Place,
London, S.W.1.
Chief Medical Officer : Dr. J. M. ROGAN
Pneumoconiosis field research

Progress continues to be made in each branch of this project, some of which is relevant to air-pollution research.

C.6 United Kingdom Atomic Energy Authority,
Industrial Group,
Windscale Works,
Sellafield,
Calderbridge,
Cumberland.
Director : K. SADDINGTON

Investigation of the general problem of filtration of radioactive material from effluent gases.

C.7 Atomic Energy Research Establishment,
Harwell,
Didcot,
Berkshire.
Director : Dr. B. F. J. SCHONLAND
Research workers : N. G. STEWART, R. N. CROOKS, R. G. D. OSMOND
Project : Transport and deposition of long-lived fission products from nuclear test explosions

Routine measurements are made of the fission product content of the atmosphere above the United Kingdom. In addition, a network of six stations in the United Kingdom and thirteen in other parts of the world has been set up at which rainwater is collected and analysed for ^{89}Sr, ^{137}Cs and ^{90}Sr. Apart from providing information of radiological importance, the object of the measurements is to study the mode of transport of weapon dust from stratosphere to troposphere and its subsequent deposition on the surface of the earth.

D. INDUSTRIAL RESEARCH ASSOCIATIONS

D.1 The British Ceramic Research Association,
Queens Road,
Penkhull,
Stoke on Trent.
Director : Dr. A. T. GREEN, C.B.E., D.Sc., F.R.I.C., F.Inst.P., M.I.Chem.E., Hon.M.Inst.Gas E., F.Inst.F., F.I.Ceram.
Secretary : T. COLLINSON

VOL. 1 958/9

The performance and efficiency of kilns and furnaces used in the ceramic industries have been evaluated. Data have been collected concerning the design and installation of smoke alarms, indicators and recorders.

D.2 The British Coal Utilization Research Association,
Randalls Road,
Leatherhead,
Surrey.
Director General: Dr. D. T. A. TOWNEND, C.B.E., Ph.D., D.Sc., D.I.C., F.R.I.C., Hon.M.Inst.Gas E., M.I.Min.E., F.Inst.F.
Director of Industrial and Domestic Development Laboratories: J. S. HALES, B.Sc., A.Inst.P. F.Inst.F., A.M.I.H.V.E.
Director of Basic Research Laboratories: R. L. BROWN, M.A., F.Inst.F., F.Inst.P.

To devise methods of measuring and controlling the emission of dust and grit from industrial appliances. To investigate the methods of reducing smoke emission from domestic heating appliances and to develop improved methods of smoke measurement. To devise methods for reducing sulphur emission from domestic fires. To develop equipment for burning small coal smokelessly in industrial and commercial boilers.

D.3 The British Coke Research Association,
74, Grosvenor Street,
London, W.1.
Director: G. W. LEE, M.Sc., F.R.I.C., F.Inst.F.
In charge of effluent research: Dr. R. L. COOPER.

The investigation of possible atmospheric pollution caused by the quenching of coke. These studies are also linked with an examination of corrosion effects resulting from this operation.

D.4 The British Internal Combustion Engine Research Association,
111–112, Buckingham Avenue,
Slough,
Buckinghamshire.
Director: Dr. W. P. MANSFIELD

A paper " Diesel combustion study by infra-red emission spectroscopy " presented by Dr. W. T. LYN in September, 1956, to the Institute of Petroleum, remotely connected with the subject of air pollution by diesel-engine exhaust gases.

D.5 The British Iron and Steel Research Association,
140, Battersea Park Road, London, S.W.11. } Laboratories.
11 Park Lane, London, W.1. } Head Office.
Director: Sir CHARLES GOODEVE, O.B.E., F.R.S.

(1) The quantities and character of the solid particles emitted to the atmosphere from processes operated at iron and steelworks are being measured. Data on the costs and efficiencies of some commercial gas-cleaning plant have been collected and are being extended. Investigations are being made into the physical character of iron-oxide fume particles and improvements are being sought to the design and operation of gas-cleaning plant. (Work carried out by R. A. GRANVILLE, W. G. JAFFREY—Physics Dept.)
(2) The causes and mechanisms of iron-oxide fume formation are being investigated and means for its prevention or reduction will be sought.
(Work carried out by Dr. E. TURKDOGAN—Chemistry Dept.)
(3) The effects of climate and pollution on the corrosion of steel are being examined.
(Work carried out by Dr. J. C. HUDSON, J. F. STANNERS, K. A. CHANDLER—Chemistry Dept.)

D.6 The British Steel Castings Research Association,
East Bank Road,
Sheffield, 2.
Director: Dr. A. H. SULLY, M.Sc., Ph.D., F.I.M., F.Inst.P.

Research on atmospheric pollution in steel foundries is concerned with two main topics:
(1) The study of respirable dust concentrations in steel foundries and the physical and chemical characteristics of these airborne dusts.
(2) The study of the iron-oxide fume produced in steelmaking in basic electric-arc furnaces.

D.7 The Motor Industry Research Association,
Lindley,
Nr. Nuneaton,
Warwickshire.
Director: Dr. A. FOGG, D.Sc., M.I.Mech.E.

Mainly coordinates research carried out by its member companies. Has also carried out experimental work on apparatus and methods for measuring the pollution caused by vehicle exhausts.

D.8 The Research Association of British Paint Colour & Varnish Manufacturers,
The Paint Research Station,
Waldgrave Road,
Teddington,
Middlesex.
Director: Dr. L. A. JORDAN

Effects of atmospheric pollution on painted surfaces.

VOL.
1
58/9

E. UNIVERSITIES

E.1 *University of Durham*
Department of Industrial Health,
King's College,
Newcastle upon Tyne, 1.
Director: Professor R. C. BROWNE, M.A., D.M., M.R.C.P.
Research Assistant: R. GRAHAM

A study is being made of the exhaust conditions resulting from running a high-speed diesel engine on low-grade residual fuels, with particular reference to the effects of inorganic fuel constituents and the associated health hazards.

E.2 *University of Durham*
Public Health Engineering Section,
Department of Civil Engineering,
King's College,
Newcastle upon Tyne, 2.
Senior Lecturer: P. C. G. ISAAC

A study will shortly be undertaken of methods of measuring airborne smoke particles.

E.3 *University of London*
Imperial College of Science and Technology,
Exhibition Road,
South Kensington,
London, S.W.7.

Department of Meteorology
Director: Professor P. A. SHEPPARD, B.Sc., F.Inst.P., with

Department of Mathematics
Reader: Dr. R. S. SCORER, M.A., Ph.D.
Research Assistant: J. M. RICHARDS

The rise of buoyant gas emitted into a horizontal stream (the bent-over plume); and the influence of vertical density stratification in the stream. Approach is through experiments conducted in a water tank (capacity 45 ft³) and a simple dimensional theory, the numerical constants for which are derived from the experiments.

E.4 *University of Sheffield*
Department of Fuel Technology and Chemical Engineering,
Mappin Street,
(St. George's Square),
Sheffield, 1.

Director: Professor M. W. THRING, M.A., F.Inst.P., F.Inst.F., M.I.Chem.E.

The Department carries on an extensive programme of research, most of which is sponsored by the Department of Scientific and Industrial Research, by the Ministry of Power or by the British Coal Utilization Research Association. Amongst the topics which have been investigated in recent years, or are now under investigation, are: the rate of combustion of gas-borne soot and the combustion of coal smoke, the mixing of secondary air over a fuel bed, the removal of sulphur dioxide from flue gases by dry methods, a study of the interrelation of sulphur oxides and soot during combustion, the smoke-producing properties of coal, reduction of fumes from steel-making furnaces, partial carbonization of lump coal, combustion of single particles of pulverized coal, and the design of an experimental high-efficiency smoke-consuming domestic open fire.

VOL
1
1958/

Int. J. Air Poll. Pergamon Press 1959. Vol. 1, pp. 249–51. Printed in Great Britain.

RESEARCH IN AIR POLLUTION IN JAPAN

Herein are listed the main institutions where *research* in air pollution is being conducted in Japan. Anyone requiring fuller information about the investigation of air pollution in Japan should communicate with Prof. Schichiro Akiya, No 1, 3-chome, Takamatsu-cho, Toshima-ku, Tokyo, Japan.

Ed.

1. Department of Public Health,
Medical School of Hokkaido University,
Sapporo N.12.W.5, Hokkaido.

Director : Professor SANSHI ABE
Research workers : HEIHACHIRO YAZAWA, RYOICHI WATANABE, FUMIO TSUNODA

Studies on atmospheric pollution in Sapporo:
(1) Effects on ultraviolet rays and sunshine.
(2) Effects on health and living costs.
(3) 3,4-benzpyrene content of the atmosphere.
(4) The relation between lung cancer and atmospheric pollution.

2. Department of Preventive Medicine and Public Health,
Osaka City University Medical School,
Asahi-machi, Abeno-ku,
Osaka.

Director : Professor KAZUYA HORIUCHI, M.D., Dr.Med. Sci.

Studies on the air pollution of cities in Japan.

3. School of Pharmacy, Osaka University,
5, 6-chome, Toneyama,
Toyonaka-City.

Director : ZEN-ICHI HORII (Dean)
Research worker : Professor CHIKATARO KAWASAKI

Estimation of dust and bacteria in air.

4. Pharmaceutical Department,
Nagoya City University,
Tanabe-dori 3-1,
Mizuho-ku,
Nagoya City.

President : REN KIMURA
Dean of Pharmaceutical Department : TAKIO NAITO
Research workers : OTOHARU ISHIZAKA (Head Professor of Hygieno-chemical Laboratory)
YOSHITARO NIIMI (Assistant Professor)
HIDEO NAGANO, HIDEKO ENDO

Studies on the air sanitation:
(1) On assay of poisonous gases in air.
(2) On hygieno-chemical estimation of dust and silica.

5. Department of Preventive Medicine and Public Health,
Keio University, Medical School,
25 Shinanomachi,
Shinjuku-ku,
Tokyo.

VOL.
1
58/9

Director : Professor SUSUMU HARASHIMA, M.D., D.P.H.
Research worker : TOSHIO TOYAMA (Assistant Professor, M.D., M.Ph.)

Evaluation of pulmonary peak flow rate and airway-resistance of selected citizens in polluted area (under planning).

6. Department of Hygiene,
Tokyo Medical and Dental University,
Yushima,
Bunkyo-ku,
Tokyo.

Director : Professor HIROMASA KITA, M.D.
Research worker : HIROSHI YAMAGUCHI

Studies on the automatic determination of atmospheric sulphur dioxide and on smog in the Tokyo area.

7. Research Institute of Industrial Medicine,
Yamaguchi Medical School,
Kogushi, Ube City,
Yamaguchi Prefecture.

Director : Professor YOSHIKATSU NOSE
Research workers : SEKIO UENO, YOSHIO KITAGAWA, MASAKO NAKAYAMA

Effects of exposure to air pollutants on community health.

8. Kanagawa Prefectural Public Health Laboratory,
3-185, Nakamura-cho,
Minami-ku,
Yokohama.

Director : TAKESHI KODAMA
Research workers : SABURO KANNO, SHOZO FUKUI, HARUO IKEDA, SHÔGO OCHIAI

New colorimetric determination of atmospheric sulphur oxides by the use of barium molybdate.

9. National Hygienic Laboratories,
2-203, Tamagawa-Yoga-machi,
Setagaya-ku,
Tokyo.

Director : Dr. TATSUO KARIYONE
Research workers : KAKUMA NAGASAWA, MASAKAZU KAWAMURA

On the radio-contamination of the air.

10. Institute of Public Health,
No. 39, 1 chome,
Shiba-shirogane-dai-machi,
Minato-ku,
Tokyo.

Director : KIYOSHI SAITO
Research workers : TAKEO SUZUKI, SEIJIRO OHTANI, SHIGEHARU KOSHI

Meteorological study of air pollution. Effects of air pollution upon man.

11. The Faculty of the Science of Living,
Osaka City University,
5-chome, Nishinagahori-Minamidori,
Nishi-ku,
Osaka.

Director : Professor HIKARU SHOJI

Public nuisance by air pollution.

VOL
1
1958/

12. Osaka Prefecture Hygienic Laboratory,
1-chome, South,
Mori-machi,
Higashinari-ku,
Osaka.

Director : KENGO MATSUOKA
Research workers : CHŪJI TAKEMI, KOYATA IIEDE, MICHIO NAGAI, YOSHIKADO MAEDA

Investigation of atmospheric pollution: Measurement of sulphur dioxide in air. Analysis of rain water and descending smog.

13. National Hygienic Laboratories,
2-203, Tamagawa-Yoga-machi,
Setagaya-ku,
Tokyo.

Director : Dr. TATSUO KARIYONE
Research workers : SHIGEHARU ICHIKAWA, GORO URAKUBO

On air pollution by the waste gases from factories in the industrial area of Tokyo.

VOL.
1
58/9

Int. J. Air Poll. Pergamon Press 1959. Vol. 1, pp. 252–54. Printed in Great Britain.

Reports on Meetings

1958 Conference of the National Society for Clean Air

Report of a conference held at Llandudno from 1 to 3 October 1958

THE major items of interest which can be reported on the 1958 Conference of the National Society for Clean Air, held in Llandudno, N. Wales, on October 1–3 are:

(1) There has been a marked reduction in the emission of smoke from industrial chimneys since June 1958, the date on which the regulations for England and Wales came into force governing permissible periods of emission of dark smoke under the British Clean Air Act 1956.* This improvement has been obtained without numerous prosecutions.

(2) There has been an absence of public demand for the establishment of Smoke Control Areas (in which all houses must burn smokeless fuels). Proposals for 182 Smoke Control Areas have nevertheless been made by 108 Local Authorities up and down the country, though they are very unevenly distributed among 7 million houses in the Black Areas. Only twenty-eight areas are in operation: they are either in city centres or in new housing estates where it is easy to make it a condition of tenancy that only smokeless fuels may be burned. A great stumbling block is that many of the Black Areas are districts where coal mining is carried out and the miners are issued with "concessionary coal" as part of their wages, a practice going back to the beginning of the coal mining industry.

(3) Approval of the height of new industrial chimneys for large plants under Section 10 of the Clean Air Act is now decided by the Cities of Leeds and Coventry on the calculated maximum ground level of SO_2. In Leeds the maximum SO_2 for a wind speed of 5 miles/hr must not exceed 40 parts per hundred million, as calculated by Sutton's formula.

(4) In the Associated Exhibition, there were shown several open grates for burning smokeless fuels which would be most unsatisfactory with the usual gas coke available to householders because the grate bar spacing was too close and the percentage free space too small. These grates are usually sold for burning either coal or coke; grates which give a really good performance with coke would give an excessive ash pit loss with coal.

Address by Minister of Housing and Local Government

The Minister of Housing and Local Government, Mr. HENRY BROOKE, reminded the Conference that Britain now had the most advanced system of air pollution control in the world and it had evoked much interest at conferences of the World Health Organization and of the Organization for European Economic Co-operation.

The administration of the Act and its associated regulations was in the hands of the Local Authorities except where there were special technical difficulties, in which case the processes were scheduled under the Alkali Act. Following a special enquiry last year, the number of such processes had been increased in 1958 from 1600 to 3400. This, of course, was a very small number compared with all the boiler and process plants coming within the general law. The number of Alkali Inspectors had been trebled and was now twenty-eight.

Although the proposals for Smoke Control Areas only amounted to 33,000 acres compared with an estimate for the whole of the Black Areas amounting to at least 3 million acres, a good start had been made and nearly all the Local Authorities in the Black Areas had adopted bye-laws requiring that fireplaces in new houses should be capable of burning coke.

Presidential Address by Dr. R. Lessing

In his address "Clean Air on the Way", Dr. LESSING said that the attitude of industry to the new legislation marked a radical reversal from that adopted in the past. Whereas the Smoke Abatement Act of 1926 had been opposed by industry, the Federation of British Industries was now co-operating to make the Clean Air Act effective. But much hard administrative work on the part of the Local Authorities would be necessary to secure a steady growth of smoke control areas in the most densely populated and highly industrialized districts. Close collaboration between adjoining Local Authori-

* For a summary of the provisions of this Act see *Int. J. Air Poll.* **1**, 120.

VO 1 1958

ties was essential: thus 103 Authorities administered the 700 square miles of Metropolitan London and hence some real executive power was highly desirable for groups of authorities.

Dr. LESSING outlined the outstanding problems on which research was required: the sulphur oxides problem with special reference to the effect on humans in the smokeless areas of the sulphur oxides arising from domestic fires using smokeless fuels; the development of better smokeless fuels which will be recognized by the ordinary housewife as giving better value than coal; improvement and cheapening of dust arrestors with easier methods of monitoring their performance; prevention of objectionable exhausts from motor vehicles.

The following sections give an account of the major points of interest which arose during the discussions.

Control of dark smoke emissions: G. W. FARQUHARSON (Chief Smoke Inspector, Birmingham).

It was doubtful whether any Local Authority would be able to check whether plants emitting dark smoke at intervals were within the sliding scale of 14–41 min allowed per 8 hr according to the number of furnaces discharging to a chimney. The system whereby temporary exemption certificates may be granted by Local Authorities pending improvements to existing plant provides an excellent opportunity for securing that really suitable modern plant adapted to the fuel will be installed. In examples of abatement notices served prior to the Act, it was shown that stricter supervision by management was the remedy required in nearly 60 per cent of 123 cases, and that estimated expenditure on improved equipment averaged £1500 for 25 per cent of the factories. Ready co-operation by owners has been obtained in most cases of contraventions of the Act.

Height of Chimneys: N. BASTABLE (Chief Public Health Inspector, Barking).

The control given to Local Authorities is intended to reduce the ill effects of emission of gases and dust from low levels. As many smoke inspectors are unaware of the theoretical work on the diffusion of gases and fine dusts from chimneys, the paper gives an account of the formulae published in this country for calculating the maximum ground level concentration of SO_2 and also outlines means for avoiding downwash. The practical application of the formulae by the City of Leeds has been given at the beginning of this report. For small heating plants there is a sliding scale ranging from 35 ft to 120 ft, the latter being for a Lancashire boiler plant.

VOL.
1
958/9

Air Pollution in London and its Smokeless Zone: T. S. PINDARD and E. J. WILKINS (Department of Scientific and Industrial Research, Fuel Research Station).

Britain's hopes of clean air depend to a large extent on the idea of the spreading smokeless zone but apathy towards the establishment of zones is encouraged by the thought that smoke from surrounding areas will pollute an island smokeless zone so much that the reduction of smoke in it will be negligible.

This paper is a first attempt to survey air pollution over a large area on the basis of one year's results. A total of 300 measuring instruments were located at carefully selected " average " sites over 150 square miles of the London area. Relatively simple and rational patterns of pollution have been obtained for insoluble deposits (dust), sulphur dioxide and smoke; for total soluble deposits the pattern was less distinct. It is suggested that surveys on these lines, in greater or less detail, would be of assistance to authorities implementing the Clean Air Act.

An attempt has been made to estimate the reduction of smoke concentration in the City of London's smokeless zone of 1 square mile. It is not possible at this stage to make a firm assessment but there are indications that the average concentration over much of the smokeless zone is about 40 per cent below that of the adjacent boroughs. Measurements of dust deposition and sulphur dioxide showed no reduction in the City but sulphur dioxide and smoke appeared to be reduced over some large open spaces.

In the papers on Smoke Control Areas it was reported that the seven boroughs north and south of Hammersmith Bridge have agreed to co-ordinate the choice of smoke control areas to provide a clean air barrier stretching north and south across West London.

Other Papers

Control of Grit and Dust Emissions by T. M. ASHFORD.

Forum of Smoke Control Areas—Reports from the Society's Divisions.

Atmospheric Pollution and Respiratory Disease by Dr. D. D. REID.
Hazards from Airborne Radioactive Matter by G. B. COURTIER.
An Automatic Smokeless Stoker for Central Heating by D. V. BROOK and S. A. BURKE.
Clean Air, Urban Amenity and the Growth of Towns by Sir WILLIAM HOLFORD (des Voeux Memorial Lecture).

The full proceedings with discussion will be published in January 1959.

Imperial Chemical Industries Ltd. GORDON NONHEBEL

VOL
1
1958/

Int. J. Air Poll. Pergamon Press 1959. Vol. 1, p. 255. Printed in Great Britain.

Atmospheric Chemistry

Report of a meeting held in London on 19 November, 1958 by the Royal Meteorological Society

A meeting was held in the rooms of the Royal Meteorological Society on 19 November, 1958 when the topic for discussion was atmospheric chemistry.

In opening the proceedings Mr. B. C. V. ODDIE welcomed the two principal speakers, Professor EGNÉR of the Institute of General and Inorganic Chemistry, Uppsala and Dr. C. E. JUNGE of the Air Force Cambridge Research Center, Massachusetts, and dealt briefly with the history of atmospheric chemistry in relation to meteorology. The term atmospheric chemistry was somewhat misleading in that the studies were almost entirely confined to the troposphere. Thanks to the energetic activities of the Swedish authorities, not least Professor EGNÉR himself, there were now 120 to 130 stations in N.W. Europe sampling rainwater and a slightly smaller number taking air samples.

Professor EGNÉR dealt with the chemical equilibrium between the air and the earth with its varying surface of soil, plant life and sea. The subject was of prime importance to agriculturists for whom the concentrations of some substances in the air as low as only 10 molecules per mm^3, butyric acid, for example, were of interest. The equilibrium problem was complex because the volatility of gas and aerosol in solution varied with temperature and with the acidity of the solution. There was, for example, a continuous distillation of sulphur dioxide from acid soils to alkaline soils while the reverse process took place for ammonia.

Dr. JUNGE concentrated his talk on two aspects:

(1) the distribution of sodium and chloride in aerosol form and

(2) the sulphur budget of the atmosphere in both aerosol and gaseous form.

In discussing aerosol distribution he stressed the importance of taking account of the size distribution. Although particles of less than $0{\cdot}1\mu$ diameter are by far the most numerous they contribute less than 10 per cent of the total mass distributed and are therefore relatively unimportant. In his investigations he used a cascade impactor to separate " large " nuclei ($0{\cdot}1\mu$ to 1μ) from " giant " nuclei and showed interesting variations between these two classes. For example, the chloride in large particles is almost certainly of continental origin but in giant particles of maritime origin (see *Tellus* **8** (2), 127, May 1956). From maps of chloride distribution over America (*Tellus* **9** (2), 164, May 1957) he deduces a half-life period of 6 days for sea salt in the atmosphere.

Concerning the sulphur budget the remarkable fact is the constancy of the hydrogen sulphide content at around 10μ g/m^3 even in highly polluted areas such as the centre of New York. The sulphur dioxide content, however, is extremely variable. Sulphur dioxide can be converted into sulphuric acid in two ways, photochemically at the rate of 0·1 to 0·2 per cent per hour and by oxidation in cloud droplets where a few per cent of the sulphur dioxide in solution is converted in a reaction controlled by the acidity of the drop. From maps of distribution of the sulphate ion Dr. JUNGE concludes that approximately 30 per cent of the sulphur arising from causes other than sea spray comes from industrial activity. Samples of ice laid down at different times in the Greenland ice-cap, however, do not show any variation in sulphate content as far back as 1915, perhaps because industrial sulphate is more readily washed out of the atmosphere than that naturally occurring. Measurements at the South Pole and elsewhere in Antarctica have given intriguing results not yet satisfactorily explained. The Cl/Na ratio is substantially less at the South Pole than the sea-water ratio and the K/Na ratio more than ten times greater.

Dr. JUNGE concluded by mentioning some preliminary results from a few free balloon flights well into the stratosphere. It appeared that the concentration of particles larger than $0{\cdot}05\mu$ was fairly constant from 10 to 30 km above ground at about 0·1 to 1·0 particles per cm^3. Particles around $0{\cdot}1\mu$ diameter were most frequent but the mass distribution increased with size at least up to 10μ, the largest particles caught. The smallest particles were hygroscopic and probably of terrestrial origin but the large particles were not hygroscopic and were probably meteoritic dust.

R. F. JONES

Meteorological Office
London, W.C.2

VOL.
1
58/9

Int. J. Air Poll. Pergamon Press 1959. Vol 1. pp. 256–57. Printed in Great Britain.

Notes and News

The air over Louisville

Summary of a joint report by the Special Air Pollution Study of Louisville and Jefferson County, Kentucky, 1956–57. 57 pp., color, illustrated (May 1958)

AN intensive study of the nature and causes of air pollution in Louisville and Jefferson County, Kentucky was conducted in 1956 and 1957 by participants from city, county, state, and federal organizations. Technical direction was by the U.S. Public Health Service.

The aims of the study were to secure the following:

(1) A complete inventory of the sources of air pollution.
(2) An air sampling program to determine air quality.
(3) A detailed meteorological study of the area.
(4) An odor and human response survey in terms of physical discomfort and dust nuisance.
(5) A study of material deterioration from air pollution.
(6) A study of seasonal variation of air-borne bacteria.

The source inventory indicates that 440 tons of pollutants per day are discharged to the air over the West End and Rubbertown; 90 per cent is gaseous (SO_2, NO_2, etc.) and 10 per cent is particulate. Nine per cent of the total is from domestic sources, six per cent from transport, and 85 per cent from industry. The quantity of each pollutant emitted by each major industry is indicated.

A study was conducted to indicate atmospheric transport of pollutants by utilizing a tracer technique employing fluorescent particles released in Rubbertown. Four tests, made under differing meteorological conditions, demonstrate their importance in determining the distribution of the pollutants at ground level.

The relationship between wind direction and air quality for airborne solids, calcium, and chlorides is given. As one example, a large source of calcium in Rubbertown causes the calcium concentration in Western Louisville to be 2½ times higher when the wind blows from Rubbertown than when it doesn't.

Three high volume particulate samples were taken at each of six stations each day for 1½ years. According to one analysis samples taken from 4.00 p.m. to midnight consistently showed concentrations of total air-borne particulate higher than during the other two-thirds of the day.

Odor thresholds of various pollutants were determined by a panel of participants as part of the human response study. These thresholds were related to the concentration of specific air pollutants measured in air samples. In the extreme case the measured concentration of one pollutant gas sample taken in Western Louisville was 25 times the odor threshold.

Several new techniques were devised during the study. One was the taking of truck-sized grab samples of air, freezing out the constituents with liquid oxygen, and determining the air pollutant concentrations for minute quantities of a variety of gaseous air pollutants with a mass spectrometer.

Results for each phase of the study are shown. Nine recommendations for alleviating the air pollution problem are listed. The report is available from the Community Air Pollution Program, Sanitary Engineering Center, U.S. Public Health Service, Cincinnati, Ohio.

RALPH I. LARSEN

Bent-over jets

The flow in a jet directed normal to the wind for values of the jet exit speed ÷ wind speed equal to 4, 6, and 8 is mapped in R. and M. No. 3074 of the Ministry of Supply, published by H.M.S.O. at 6s. 6d.

The paper describes briefly the experimental results of R. Jordinson obtained in a wind tunnel in the Department of Aeronautics at Imperial College. Plane sections of the jet at various distances downstream are represented by maps of the total head of pressure, and the horseshoe shape of the sections when the jet is bent over is clearly seen.

The use of maps of air speed to obtain a picture of the jet is open to the objection that it will not

necessarily give a picture similar to that obtained from measurements of concentration of effluent. Since we do not properly understand the mechanisms whereby the momentum of the jet and its environment are exchanged, the author's brief interpretive comments on his findings should be regarded as suggestions only; but this in no way detracts from the value of the observations.

The results should at least be noted by anyone working on the difficult theoretical problems of bent-over jets and plumes.

R. S. SCORER

Basic Research on Aerosols in the U.S.S.R.

BASIC research on aerosols in the U.S.S.R. has a long tradition. As early as 1882 Academician V. SREZNIEVSKI published his law of evaporation of aerosol drops. However, the main theoretical as well as experimental development in the sphere of aerosols began in the Thirties of this century when Professor NIKOLAJ ALBERTOVITCH FUCHS, jointly with Professor IVAN VASILIEVITCH PETRYANOV, published their work on the measurement of electrical charges on aerosols and the influence of the charge on the mechanics of an aerosol cloud. Both these research workers were members of the Karpov Institute of Physical Chemistry in Moscow at that time. Only a few years later, B. V. DERYAGIN and P. S. PROKOROV organized a working team for research on aerosols at the Institute of Physical Chemistry of the Academy of Sciences. After World War II, rapid development in aerosol research began in both these institutes. Although Professor N. A. FUCHS has left the Karpov Institute of Physical Chemistry to become editor of the journal *Referativnij zurnal pro chimii* at the Institute of Scientific Information of the Academy of Sciences, notwithstanding, he has remained faithful to his aerosols. His new field of activity enables him to keep in touch with literature concerning aerosols from all parts of the world, and to work theoretically. At present he is recognized as a leading theoretician on the subject of aerosols. His book *Mechanika aerozolej* (Publishing Office of Akademia Nauk, Moscow, 1955) is the first theoretical text-book on aerosols in the whole world. The subject "Mechanics of aerosols" itself has been introduced by FUCHS as a subject following laws of dynamics of the aerosol cloud. His latest theoretical monograph *The evaporation and growth of drops in the gas medium* (*Isparenje i rost kapelek v gazoobratnoj srede*) is also considered a new contribution to the theory of liquid aerosols. Professor FUCHS is nowadays also carrying out much experimental work, to fill gaps still existing in the theory of aerosol thermophoresis (movement of particles in a thermal gradient). FUCH's first pupil and collaborator, Professor J. V. PETRYANOV, is still working in the Karpov Institute; he directs the work in his laboratory on the investigation of aerosols and air-filtration. Professor PETRYANOV and his group have developed a method for the production of filters of very fine fibres of dielectric materials.

VOL.
1
58/9

The efficiency of these filters, determined by optical methods, amounts to 99,99–99,999 per cent with a minimum resistance. These filters have been in practical use for three years (in the nuclear industry, in the metallurgy of coloured metals, in industrial hygiene, sterilization of air, etc.).

The working group engaged in research on aerosols in the Institute of Physical Chemistry of the Academy of Sciences is directed by P. S. PROKOROV, Doctor of Chemical Sciences. This working team has been essentially interested in three branches of aerosol research, namely, meteorological effects on the origin, growth, and coagulation of liquid aerosols; problems of moistening (wetting) solid aerosols (primarily industrial aerosols), and last, analytical methods of following the concentration and dispersion of aerosols.

The theoretical developments by B. V. DERYAGIN and his research fellows on the character and role of surface forces on the kinetics of dispersive systems are of world importance. This work was published in 1956 and 1957 in the Documents of the Academy of Sciences (*Dokl. Akad. Nauk S.S.S.R.*).

A number of research institutes and laboratories are concerned with applied research on aerosols, studying their applications in medicine, agriculture, and meteorology, as well as the ways of combating toxic, biological and radioactive aerosols.

K. SPURNÝ

Int. J. Air Poll. Pergamon Press 1959. Vol. 1, pp. 258–60. Printed in Great Britain.

Book Reviews

Air Pollution Control in New Jersey. Progress Report. New Jersey Air Pollution Commission 28 pp.
P. A. KENLINE: **Appraisal of Air Pollution in Tennessee.** U.S. Dept. of Health, Education and Welfare, 1957. v + 85 pp.

WHILE in the U.S. I had occasion, more than once, to drive along the Pulaski Skyway into New Jersey. This road among the industrial chimneys and gasburners gave the impression of passing over the jaws of hell. It is good to know, therefore, that in 1954 the legislature of New Jersey passed its Air Pollution Control Act.

Health departments in Britain are in the habit of carrying out most of their control functions by advice and admonition, rather than by prosecution. They have not—except in very rare cases—pursued this co-operative attitude to its useful conclusion and co-opted the poachers onto the panel of gamekeepers. In America, however, with its later start in environmental control, there is a greater sense of urgency, and industry (there the main air polluter) is prominently represented on the New Jersey Air Pollution Control Commission, providing its chairman amongst others. It is, indeed, clear that, in New Jersey, industry was in the forefront of public opinion in the campaign for clean air.

The Commission is responsible for the preparation and promulgation of the detailed regulations controlling air pollution. These regulations are made only after public conference and formal inquiry. Regulations so far promulgated cover air pollution from open-air burning of refuse, smoke, and air pollution from the combustion of solid fuel. The Commission also organizes County Air Pollution Control Associations.

The actual work of control is carried out by a division of the State Department of Health, the so-called Air Sanitation Program, which has three sections: enforcement, technical service and special investigation, and research and development. The enforcement section deals with the "policing" of the regulations; samples are taken and measurements made by the technical section which also carries out field studies.

Section 14 of the Act is interesting in requiring the Health Department, before going to law to control a violation, to "endeavour to eliminate any source or cause of air pollution resulting from such violation by conference, conciliation and persuasion." For the more complex industrial aerial wastes this provision demands that the Health Department shall have on its staff highly qualified men who can talk with authority to industrial technologists. Similar reasoning impels me to wish that Local Authorities in Britain would form Joint Boards for the control of air pollution, sufficiently large to provide the expert technical personnel required; the day-to-day policing could remain in the hands of the Health Departments. Already much air-pollution abatement is in the hands of an agency of central government, the Alkali Inspectorate, and it seems as though parish-pumpery may allow local government to become increasingly unfit to deal with technically complex matters.

The U.S. Public Health Service is very different from the British Ministry of Health in two important ways: it has almost no executive responsibility for public-health control and it has relatively huge funds at its disposal. The second report under notice is an example of the useful way in which the Service assists the cause of public health in America.

Tennessee has, at present, no state law to control air pollution and its Department of Public Health accordingly called in the U.S.P.H.S. to survey the extent and seriousness of air pollution in the state and to make recommendations. Air-pollution problems exist in many areas of the state, especially in the east where industry tends to congregate and where climate and topography aggravate the ill-effects of pollution. Time and time again when reading of air pollution in America it is clear that burning of refuse on open dumps or in backyard incinerators is a major contributor. In this respect, at least, Britain's municipal services are ahead of those in very many parts of the U.S.

These reports are two only from among very many from the U.S.A. which show the public interest in air pollution and demonstrate the pressure of public opinion for its abatement.

PETER C. G. ISAAC

M. DIEM and R. TRAPPENBERG: **Berechnung der Ausbreitung von Staub und Gas.** Forschungsberichte des Wirtschafts-und Verkehrsministeriums Nordrhein-Westfalen Nr 502. (Edited by Leo Brandt.) Westdeutscher Verlag, Köln, 1957. 17pp. + 67 graphs, 37.70 DM.

A certain part of the research work carried out under the sponsorship of the German Committee " Reinhaltung der Luft " is devoted to the problems of atmospheric diffusion. The calculation of the concentration of gases and dusts emitted continuously from a point source of constant strength is considered to be of great importance to the engineer when designing a new plant. On the other hand, future legislative work might depend on the reliability of the equations provided by the meteorologist.

A further attempt to give such values to the man in practice has been made by the authors. They have taken the well-known Sutton formula for calculation of concentrations near the ground. From this formula the distance of the maximum concentration at the ground is obtained. To account for changes in windspeed and for fluctuations in the horizontal wind-direction a mean value is calculated for a rectangular area of 1000 m length in wind direction and of 500 m width in crosswind direction by integrating over this area. The centre of the rectangular area is placed on the theoretical point of maximum concentration. If changes of the horizontal wind-direction are very large (i.e. the fluctuating plume will sometimes move out of the considered area) an additional correction factor is introduced.

On 66 graphs the mean-maximum concentrations so obtained and their distances from the source are shown in relation to the source strength. On each graph the parameters n (for the vertical wind-profile), v (for the horizontal mean-wind-velocity) and C_z (the " virtual " vertical diffusion coefficient after Sutton) are combined to allow for calculations in different meteorological situations. The horizontal diffusion coefficient C_y is kept constant.

The authors emphasize that the published graphs can only be used with certain restrictions to calculate the concentrations of gases. The meteorological parameters n, v, C_z must be measured at different places to allow for predictions of the frequency of certain extreme values. One can discuss the way of forming time mean values by averaging over a certain area, but after all, it is considered to be an attempt to fulfill the urgent requirements put forward by the industrial engineers.

W. KLUG

VOL.
1
958/9

D. BIENSTOCK, L. W. BRUNN, E. M. MURPHY and H. E. BENSON: **Sulphur Dioxide—Its Chemistry and Removal from Industrial Gases.** United States Bureau of Mines Information Circular 7836. 1958.

IT is about thirty years since the problem of pollution of the air by sulphur compounds and the possibility of the removal of sulphur dioxide from the flue gases of electricity generating stations was first given serious consideration. The pioneering work by the former London Power Co., which led to the development of the Battersea Process, and the work by James Howden Ltd. and Imperial Chemical Industries which led to the development of the process used at Fulham Power Station was carried out in the early 1930s. At the same time, the supply industry in the United States sponsored research on this subject, but the investigations did not lead to flue gas washing being practised in a power station.

Since the development of the Battersea and Howden–I.C.I. processes, many other processes have been tried on an experimental scale in the United Kingdom and abroad, and investigations are continuing.

The United States Bureau of Mines has recently published Information Circular 7836, 1958, by D. BIENSTOCK, *et al.*

This report contains (1) descriptions of the two processes—the Battersea and Howden–I.C.I. processes—which have operated on a full scale; (2) descriptions of processes which have been investigated on a pilot-plant scale; (3) processes which have been used to recover sulphur dioxide from gases, such as smelter gases, which contain a higher concentration of sulphur dioxide than flue gases; (4) a survey of the literature relating to the chemistry of sulphur dioxide and (5) tables of the physical properties of sulphur dioxide.

The report is a comprehensive survey of work in this field and it contains an exhaustive bibliography. A reference to recent work carried out in Russia has, however, been omitted. This work

was described in a book by N. G. ZALOGIN and S. M. SHUKHER—*Flue Gas Cleaning* (*Ochistka Dymovykh Gazov*), 2nd edition. Gosenergoizdat, Moscow, 1954. 224 pp.

The report was prepared in order to assist the personnel of the Bureau of Mines engaged in the project of studying possible methods of recovering sulphur from waste gases. It will be very useful to others interested in this problem.

H. E. NEWALL

VO
1
1958

PAPERS TO BE PUBLISHED IN FUTURE ISSUES

T. A. RICH: The average size of sub-micron particles.

W. F. CAREY: Atmospheric deposits in Britain—a study of dinginess.

Smokeless fuels from high-volatile coals.

Part I. The production of smokeless fuels by the mild devolatilization of a high-volatile coal, by D. H. GREGORY and W. N. ADAMS.

Part II. The smoke emission of low-temperature chars prepared from high-volatile coals, by A. F. GAINS and G. J. PITT.

L. W. POLLAK: Counting of Aitken nuclei and application of the counting results.

R. E. MUNN: Application of an air-pollution climatology to town planning.

VOL.
1
958/9

VOL
1
1958/

Int. J. Air Poll. Pergamon Press 1959. Vol. 1, pp. 263–265. Printed in Great Britain.

SMOKELESS FUELS FROM HIGH-VOLATILE COALS—I

THE PRODUCTION OF SMOKELESS FUELS BY THE MILD DEVOLATILIZATION OF A HIGH-VOLATILE COAL

D. H. Gregory and W. N. Adams
The Coal Research Establishment, Stoke Orchard, Cheltenham, Glos.
(*Received* 29 *December* 1958)

Abstract—With the progressive implementation of the Clean Air Act the unsatisfied demand for smokeless fuels in Britain will increase steadily and should reach several million tons per annum. During the past few years the National Coal Board has carried out at the Coal Research Establishment a considerable amount of research into the development of new processes for the production of smokeless fuels. In one of these processes a char formed by devolatilization of high-volatile coals in a fluid bed at about 425° C is subsequently briquetted. Although this fuel contains more than 20 per cent of volatile matter it is effectively smokeless. The process is described in the first part of the present paper; the second part describes fundamental work into the cause of the marked reduction in smoke emission resulting from this mild devolatilization of the coal.

1. INTRODUCTION

In the Clean Air Act, the Smoke Control Areas (Authorised Fuels) Regulations 1956, No. 2023, low-volatile steam coals are among the approved smokeless fuels. These coals have a range of volatile matter of 9·1 per cent to 19·5 per cent, while the other approved fuels such as Phurnacite, Coalite, Rexco and gas coke, referred to in the Act have volatile matters near or less than the lower limit of this range. It may be assumed that manufactured fuels having higher volatile matters than 19·5 per cent are not debarred provided their smoke emission is not greater than a coal of this volatile matter. That is, the criterion of acceptance as a smokeless fuel is logically smoke emission and not volatile matter.

Careful consideration has been given to the types of coal which should be used as raw materials for the production of smokeless fuel. The quantity of naturally smokeless coal is very limited, occurrence and output being restricted to South Wales, Kent and to parts of Durham and Scotland. Many other types of coal have specialized uses in, for example, the iron and steel industry and in the gas industry. The freely available coals for smokeless fuels are the smaller sizes of the high-volatile Midlands coals, and attention has therefore been concentrated on these.

2. DEVOLATILIZATION

R. J. Piersol (1936) showed that, to make certain high-volatile American coals smokeless, the volatile matter had to be reduced by only about 15 per cent; and this, he showed, could be done by a mild devolatilization. The process Piersol described, however, has not been developed to a commercial scale.

At the Coal Research Establishment it has been shown that British coals of high-volatile matter can also be made smokeless by removing only a relatively small part of the coal substance. The relation of smoke emission of a char to its volatile matter is given in Fig. 1 for three different high-volatile coals. It is seen that for each coal the

VOL. 1 58/9

smoke emission is reduced rapidly as the volatile matter is decreased, and becomes practically zero when the volatile matter is reduced to about 23 per cent. The solid yield on the dry basis of this mild carbonization is very high at 80 per cent to 85 per cent.

A fluidization technique has been developed to achieve the mild devolatilization necessary to produce a smokeless char. The technique of fluidized carbonization is well known and has been described elsewhere in British and American literature. It is similar in broad outline to the technique of fluidized catalytic cracking, but differs in that the solid is fed into and withdrawn from the reactor continuously, whereas in cracking the solid catalyst is recirculated. Moreover, the chemical reaction occurs in

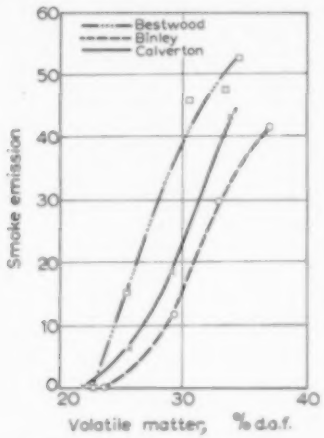

FIG. 1. Relationship between smoke emission and volatile matter content for chars prepared from high-volatile coals.

the solid and not in the gas phase. The main advantages which a process of this kind has over conventional methods of carbonization are that it is continuous, and that it is adaptable to automatic and strict control of carbonizing temperatures, so giving a uniform product not readily obtainable by batch operation. Another advantage is that high heat-transfer rates are also achieved.

With such a novel method of carbonization it is essential to proceed through a number of stages of development from the laboratory scale to pilot plants with a throughput of perhaps 1 ton/hr to a demonstration plant of about 100 ton/day. A small pilot plant of 1 ton/day capacity has been in operation for some years and one of 1 ton/hr capacity will shortly be working. Further stages of development are under consideration.

3. BRIQUETTING

The product from the carbonization process is, of course, still a powder and as such could not be used on a domestic grate. Attempts to convert smokeless powdered char into a sized fuel without destroying its smokeless properties have been made by other workers (DARMONT, 1952; HARDY, 1933).

In the main, briquetting with binders has been employed but none of the methods suggested has been developed on a commercial scale, mainly because the binders

employed were not fluid over a sufficiently wide temperature range. This in turn demanded a very close control of the carbonizing temperature, a condition which could not be achieved in the units employed. At the Coal Research Establishment a process of briquetting the char with a special binder is being developed. On a 1 ton/day scale, char is briquetted in a double-roll press of conventional design with a binder consisting of coal to which pitch is added to decrease its softening point and increase its fluidity. The briquetting operation is carried out at temperatures just below the carbonizing temperature, that is, at about 350°C to 400°C.

4. SMOKE EMISSION CHARACTERISTICS OF THE BRIQUETTES

In spite of the addition of these smoky binder constituents, the result of the briquetting process is a shaped fuel having smoke characteristics similar to those of the char. The results of smoke emission tests in which such briquettes were burned on an open grate under standardized conditions are given in Table 1. The amounts of smoke evolved from briquettes formed from all the chars carbonized in the temperature range 375°C to 425°C are less than that evolved from a coal of 18 per cent volatile matter. For briquettes formed from chars prepared at 400°C and 425°C the smoke was less than that of a 15 per cent volatile matter coal.

Work still remains to be done in developing the combined process of fluidized carbonization and hot briquetting to the full production scale, but the work so far has shown that technically the process is sound and that it has produced a satisfactory smokeless fuel for the open domestic grate.

TABLE 1. SMOKE CHARACTERISTICS IN GRATE TESTS OF BRIQUETTES MADE FROM CHARS PREPARED FROM CALVERTON COAL

Details of Char			
Carbonizing temperature (°C)	375	400	425
Volatile matter, (%, d.a.f.)	33·8	29·0	25·7
Briquetting temperature (°C)	350	375	400
Smoke emission (electrostatic method) during grate test on briquettes (wt.%)	0·77	0·39	0·27

Smoke emission (electrostatic method)	
18% volatile matter (d.a.f.) Welsh Steam Coal	1·12
15% " " " " " "	0·55

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VOL. 1 58/9

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SMOKELESS FUELS FROM HIGH-VOLATILE COALS—II

THE SMOKE EMISSION OF LOW-TEMPERATURE CHARS PREPARED FROM HIGH-VOLATILE COALS

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(*Received* 29 *December* 1958)

Abstract—In order to investigate the mechanism whereby a smokeless char is obtainable by relatively mild carbonization of a high-volatile coal, a series of chars covering a range of volatile contents has been prepared by fluidized carbonization. The amounts of smoke emitted by these chars and by coals of similar volatile contents have been measured gravimetrically in a smoke-meter, and compared with the yields of tar obtained when the chars and coals were subjected to Gray–King assay.

It is shown that the smoke emitted from coals and chars consists mainly of unburnt tarry material. The amount of smoke emitted decreases with decreasing volatile content, but is less from a char than from a coal of the same volatile content. There is however a common relationship between smoke yield on combustion and tar yield by a Gray–King assay for coals and chars. It is concluded that a char emits less smoke than a coal of the same volatile content because its tar yield is smaller. This is mainly due to the fact that during the low temperature carbonization of the parent coal, a considerable amount of tar is driven off.

It is also shown that a second factor contributes to the low tar yield of a smokeless char. As a result of the low temperature carbonization of the coal, certain pyrolysis products, which would contribute to the smoke if the coal was burned, undergo polymerization or condensation reactions to give solid products which do not yield smoke when the char is burned. The contribution from this cause towards the low tar yield of a smokeless char is, however, small compared with that arising from the evolution of tar during the low temperature carbonization of the coal.

1. INTRODUCTION

THE first part of this paper showed that a smokeless fuel of volatile content exceeding 20 per cent could be obtained from a high-volatile coal by fluidized carbonization at a comparatively low temperature. The present part of the paper describes a fundamental investigation into the cause of the marked reduction in smoke emission so obtained.

The emission of smoke from coal when it is burned is associated with the evolution of tar which has escaped combustion. Thus, BRADBURY and MOTT (1941) showed that for three coals, heated under conditions of incomplete combustion, the amount of smoke evolved is nearly equal to the corresponding tar yield as determined by a Gray–King assay. From results relating the smoke emission of chars and coals to their volatile contents, PIERSOL (1936) concluded that most of the smoke-producing constituents of the volatile matter of coal originate in the fraction released by low-temperature carbonization. This conclusion, however, can be interpreted in two ways. The first is that most of the tar is removed by the low-temperature carbonization; the second is that certain constituents of the tar are mainly responsible for the smoke, and these are evolved preferentially at the lower temperatures. The present investigation was carried out in order to gain a better understanding of the mechanism.

2. EXPERIMENTAL

2.1 *General survey*

A series of chars of different volatile contents was prepared by the fluidized carbonization of a high-volatile coal. In an exploratory set of experiments, the amount of smoke emitted by these chars was measured gravimetrically with a smoke-meter based on a British Coal Utilisation Research Association design. By this means the relationship between the smoke emission and the volatile contents of the chars was determined; information was also obtained about the composition of the smoke and the temperature of the char at which smoke was first emitted.

If the reduction in smoke emission of a high-volatile coal on mild carbonization is due to the quantity of tar removed, and not to any particular constituent, then there should be a correlation between the smoke emission and the tar yield of a char. A similar correlation should apply to coals of different volatile contents. In order to test this hypothesis, the smoke emission and the corresponding tar yields of a series of coals and chars were measured. As a test of the alternative hypothesis that the smoke is due to certain constituents of the tar which are preferentially evolved at the low temperatures of carbonization, samples of tar obtained by carbonization of the parent coal and subsequent carbonization of the char were analysed and compared.

Details of the materials, apparatus and experimental methods are given in the following sections, 2.2 to 2.5.

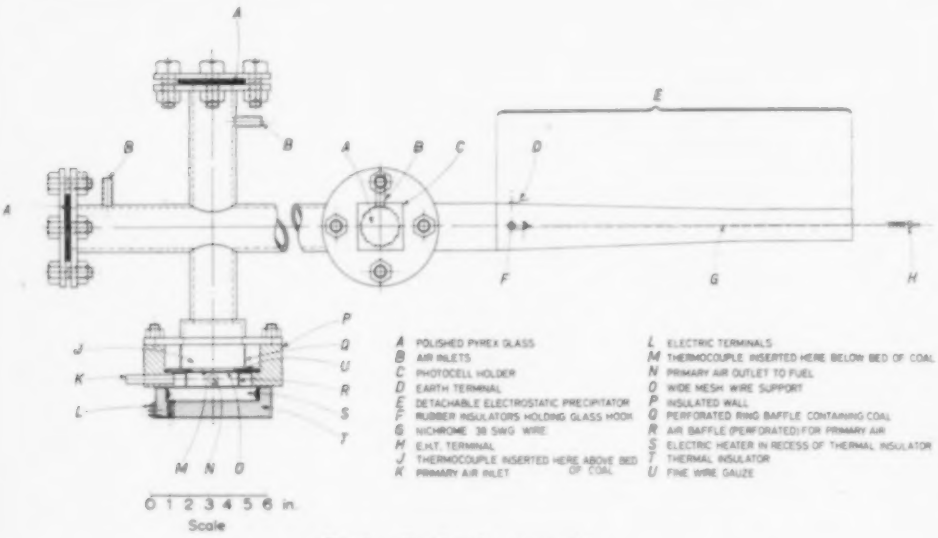

FIG 1. Combustion apparatus.

2.2 *Materials*

The series of chars covering a fairly wide range of volatile content was prepared by fluidized carbonization of a high-volatile coal (Cannock Wood, CRC. No. 802) in a 2 in. diameter stainless-steel reactor. The series of coals, used for comparison, ranged in volatile content from 18·9 to 38·8% d.a.f. In order to avoid any influence of size distribution, all the measurements of smoke emission and tar yield were made on sized fractions 10 to 30 B.S.S. The proximate analyses of these fractions are given in Table 1.

2.3 *Smoke-meter*

The design of the apparatus (Fig. 1) was based on that of FINCH and RAFTERY (1957), the principal modification being that the chimney was horizontal. This facilitated the connection of the electrostatic precipitator to a high-voltage generator.

TABLE 1. ANALYSES OF COALS AND CHARS USED

	Moisture (% as received)	Ash (% as received)	Volatile Matter (% d.a.f.)	N.C.B. Coal Rank Code No.	Fluidizing Gas
Coal					
Cannock Wood	12·8	5·6	38·8	802	
Rossington Brights	5·5	4·0	37·3	702	
Union, Hilltop Drift	0·8	16·5	29·2	301	
Cwm Mildred	0·9	4·9	24·4	301	
Bargoed	1·1	4·3	18·9	204	
Char					
(from Cannock Wood Coal)	2·9	5·1	34·0		N_2
	3·3	7·4	32·6		Air
	2·4	6·4	31·8		N_2
	2·7	7·5	29·6		Air
	2·5	6·0	28·9		N_2
	2·8	7·4	28·1		Air
	1·8	5·8	27·6		N_2
	2·2	7·5	27·5		N_2
	2·6	7·3	23·4		Air
	2·8	7·9	22·9		Air
	2·4	7·7	22·7		N_2

The bed of fuel was supported on a copper gauze disc which was replaced after each run. Heat was supplied electrically from below, and primary air was passed up through the bed at a controlled rate. No secondary air was used immediately above the fuel-bed but small amounts of air (3·2 l./min total) were introduced in front of the glass windows to prevent fogging. Thermocouples were used to measure the temperature at the centres of the upper and lower surfaces of the bed.

The presence of smoke in the chimney was detected by means of a lamp and photocell placed so that a beam of white light traversed the path of the gas. The chimney terminated in an electrostatic precipitator consisting of an earthed aluminium cylinder and an insulated axial wire maintained at +8 kV. The smoke passed between the wire and the cylinder and was precipitated completely, the yield of smoke in an experiment being determined by the increase in weight of the cylinder and wire. The contents of the precipitator were washed out with acetone for further examination.

A charge of 13g of coal or char was used in each experiment; this formed a bed about 6 mm deep. Heat was supplied at a uniform rate throughout the combustion until 5 min after optical measurements indicated that no more smoke was being evolved. If no smoke was registered optically, the heating period was 30 min.

In the exploratory experiments undertaken to study the relationship between the smoke emission and the volatile content of the chars, two different flow rates of primary air (19 and 8·5 l./min respectively) were used. The smoke collected in the electrostatic precipitator was weighed and analysed to determine the amount soluble in acetone and the dry tar content. The temperatures at the top and bottom of the fuel bed were recorded at regular intervals, and the times at which smoke and flames first appeared were noted.

For the subsequent work on the relationship between smoke emission and tar yield, the conditions of combustion in the smoke-meter were slightly modified: the flow rate of primary air was 9·7 l./min and the fuel bed was tamped to pack the particles more tightly.

2.4 *Assays*

The tar yields of the coals and chars used were measured in a standard Gray–King apparatus. Preliminary runs were performed on the coal under test to provide sufficient gas to displace the air

from the furnace tube, so that the carbonization was carried out in an atmosphere of the gas produced by that sample. The temperature of the furnace was 300°C when the tube was inserted, and was raised to 600°C at 3°C/min. Yields of char, tar, liquor and gas were measured.

The Gray–King assay was also used to compare the tar evolved in the production of a smokeless char with that evolved in its subsequent recarbonization to a higher temperature. The temperature of the coal was raised from 300°C to 425°C at 5°C/min, and held at 425°C for 30 min. The char was then reheated from 300°C to 550°C at 5°C/min and kept at 550°C for 30 min. The yields of char, tar, liquor and gas were measured in each stage. A second sample of the coal was used to determine the yields of products on heating from 300°C to 550°C at 5°C/min and maintaining at 550°C for 30 min.

2.5 *Thermogravimetric measurements*

Measurements of the loss in weight of coals and chars while being heated from 300°C to 600°C at 3°C/min were made in an apparatus similar to that described by B.C.R.A. (1948).

3. RESULTS AND DISCUSSION

3.1 *The Smoke Emission of Chars*

The variation of the smoke emission with the volatile content for the Cannock Wood chars is shown in Fig. 2. For each char two mean values of the smoke emission are plotted; these correspond to the two air flow-rates used during the smoke measurements.

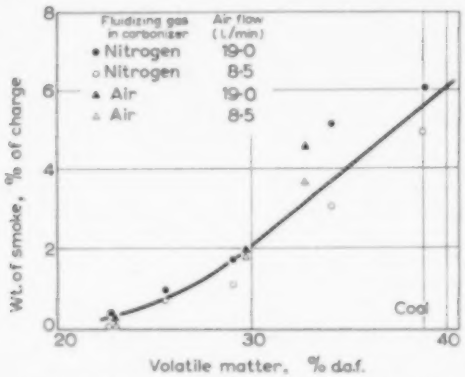

FIG. 2. Variation of weight of smoke with volatile matter content.

As shown in Fig. 2, there was a greater yield of smoke at the higher air flow-rate. For a given flow-rate, the smoke emission decreased with decreasing volatile content of the char, and became very small when the volatile content was reduced to 23 per cent. The smoke emission did not depend significantly on the fluidizing gas used in the preparation of the char.

The smoke emitted during the combustion of each char was collected in the electrostatic precipitator as a yellow tarry film which was almost completely soluble in acetone. The percentage of insoluble material did not vary significantly with the volatile content of the char. Moreover, it was practically independent of the air flow used, even though luminous diffusion flames were observed above the fuel bed during the later stages of the combustion with the higher flow-rate. The mean value, for eighteen experiments, of the percentage of smoke insoluble in acetone was 2·6 per cent with a standard error of 0·3 per cent. Semi-micro distillation of the acetone solutions showed that the average moisture content of the smoke was 6·7 per cent. Thus under the

VOL. 1 958/9

conditions of combustion used in this work, the smoke emitted by the chars was mainly distillation smoke, i.e. tar-like pyrolysis products which had escaped complete combustion.

3.2 *The relationship between tar yield and smoke emission*

As shown in Fig. 3, the amount of tar evolved from a char is considerably less than that from a coal of the same volatile content. There is a corresponding difference between the smoke emission of chars and coals, as shown in Fig. 4; for a coal and char of the same volatile content, the smoke emission is much smaller for the char.

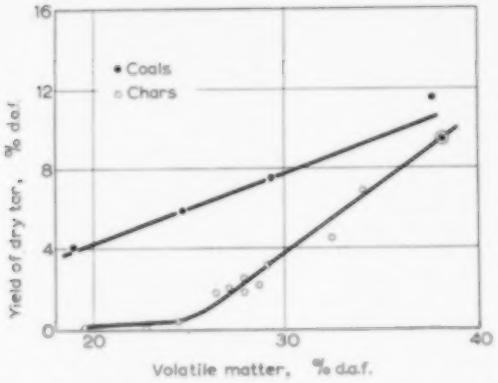

FIG. 3. Comparison of tar yields from coals and chars of various volatile matter contents.

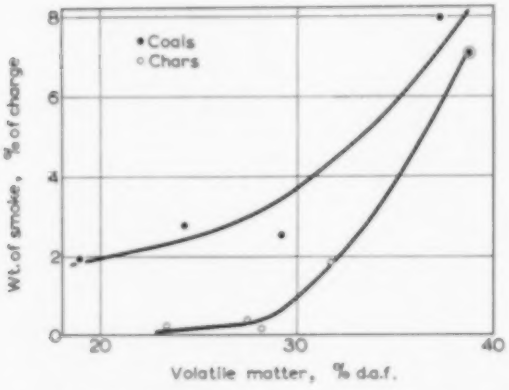

FIG. 4. Relation between smoke emission and volatile matter content.

However, the relationship between the smoke emission and the tar yield is approximately the same for the coals and chars (Fig. 5). This shows that the smoke emission of chars and coals is determined not by any particular constituent in the tar, but mainly by the total amount of tar evolved.

Further evidence for this conclusion was obtained from the analyses of the tar evolved during the initial devolatilization of the coal and of that evolved during the

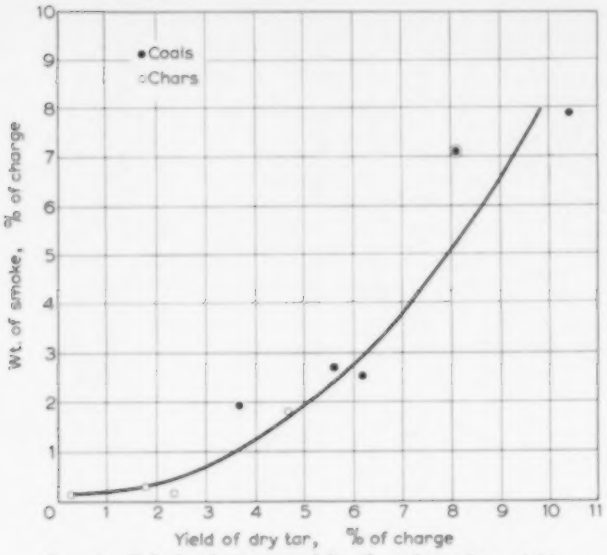

FIG. 5. Relation between weight of smoke and tar yield.

subsequent carbonization of the char (Section 3.4). The characters of these two tars were very similar.

The smoke emission was negligible for chars which yielded on carbonization less than about 2 per cent by weight of tar. It is concluded that amounts of tar up to this limit were burned under the conditions of the smoke emission measurements, but that larger amounts escaped combustion.

3.3 *The temperature of the chars during smoke emission*

During the smoke emission, the temperatures at the top and base of the bed of char were recorded. Although the reproducibility was poor, the results obtained gave further insight into the mechanism of smoke emission.

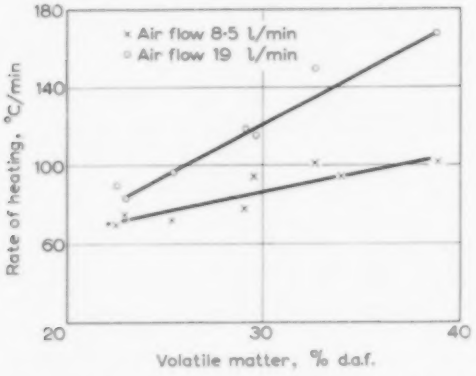

FIG. 6. Maximum rate of heating at base of bed for chars of various volatile matter contents.

VOL. 1 58/9

The maximum rates of heating at the base and the top of the bed both increased with increasing volatile content of the char, the results for the base being shown in Fig. 6. Moreover, for a given volatile content the rate of heating was greater with the higher air flow than with the lower one. This difference is probably responsible for the higher smoke emission at the higher air flow. The smoke emitted consisted mainly of tar which had escaped combustion, and, as WARREN (1938) has shown, an increase in the rate of heating results in an increase in the tar yield. Although some of the extra tar produced at the higher rate of heating will presumably be burned, the remainder will increase the smoke yield.

The temperature of the base of the fuel bed at the commencement of smoke emission varied considerably from one experiment to another. It did not, however, show any significant dependence on either the volatile content of the char or the rate of air flow through the bed, the mean value being 418°C. Thermogravimetric measurements were made on the same chars to determine the temperatures at which the volatile emission first became appreciable, i.e. a rate of loss in weight of 0·05 per cent/min occurred. These measurements were necessarily carried out at a heating rate considerably lower (3°C/min) than that of the smoke emission tests.

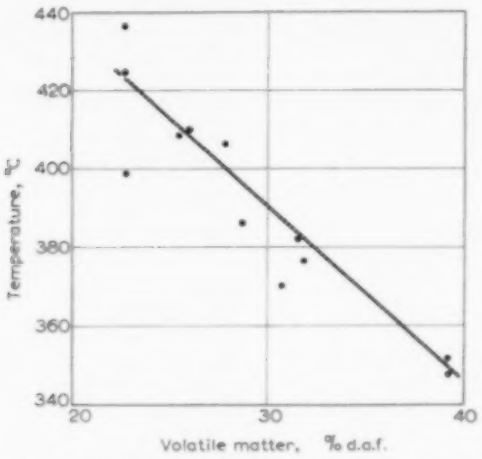

FIG. 7. Effect of volatile matter content on the temperature at which the weight loss becomes 0·05%/min.

The results (Fig. 7) show that the temperature of initial volatile evolution increased as the volatile content of the char decreased, but was generally lower than the temperature of initial smoke emission. This difference can be largely accounted for by the difference in heating rates. VAN KREVELEN *et al.* (1951) have shown that devolatilization curves, relating the loss in weight to temperature, are steadily displaced to higher temperatures as the heating rate is increased. Thus the high heating rates in the smoke emission tests will cause the temperature of initial devolatilization to be higher than that in the thermogravimetric measurements. Calculations have shown that when allowance is made for the difference in heating rates, the temperatures of initial devolatilization are much less dependent on the volatile content of the char, and close to the mean value observed for initial smoke emission.

3.4 *The tar yield of a smokeless char*

It has been shown that the smoke emission of a coal or char is determined by the amount of tar evolved on carbonization. The low smoke emission of a char arises mainly from the fact that during the initial devolatilization of the parent coal, a considerable amount of tar is driven off. Nevertheless, a higher yield of tar is evolved when the coal is carbonized to a higher temperature than that at which a smokeless char is produced. It was of interest to determine whether the increase in the yield of tar obtained on carbonizing the coal to the higher temperature corresponded to the yield of tar evolved when the smokeless char was carbonized to the same temperature.

When Cannock Wood coal was carbonized at 5°C/min to 425°C to give a smokeless char, the tar yield was 6·7 per cent by weight. Carbonization of the coal under the same conditions but to 550°C (a temperature sufficiently high for the maximum yield of tar under these carbonizing conditions) gave a tar yield of 9·8 per cent. It might therefore be expected that the yield of tar obtained by carbonizing the smokeless char to 550°C would equal the difference, namely 3·1 per cent. The yield obtained (1·8 per cent) was significantly lower. Moreover, as shown in Table 2, this decrease in the tar yield was accompanied by an increase in the yield of char, the liquor and gas yields not being significantly changed. It is therefore concluded that two factors are operative in reducing the smoke emission of a high-volatile coal by low-temperature carbonization. First, a large part of the tar is evolved during the carbonization, and secondly some pyrolysis products which would have been evolved as tar under different carbonizing conditions are converted into char.

VOL. 1 58/9

TABLE 2. YIELDS OF PRODUCTS FROM THE CARBONIZATION OF CANNOCK WOOD COAL
(percentages of dry coal)

Carbonizing conditions	Char		Tar		Liquor		Gas		Loss
	m	σ	m	σ	m	σ	m	σ	
(1) Coal carbonized to 425°C	87·7	0·25	6·7	0·19	3·8	0·42	1·4	0·03	0·4
(2) Char from (1) recarbonized to 550°C	77·8	0·15	1·8	0·11	4·0	0·12	4·0	0·24	0·1
(3) Total yields from (1) and (2)	77·8	0·28	8·5	0·21	7·8	0·43	5·4	0·24	0·5
(4) Coal carbonized to 550°C	76·8	0·34	9·8	0·11	7·1	0·08	6·2	0·22	0·1

m = mean; σ = standard deviation of a single determination.

Several workers studying different aspects of coal pyrolysis have also observed that when the upper temperature limit of carbonization is fixed, the yields of tar and char depend on the carbonizing conditions. Thus WARREN (1938) found that the yield of tar increased and that of coke decreased with increasing rate of heating of the coal. He explained this on the hypothesis that some of the intermediate pyrolysis products could undergo two alternative reactions—either evolution as tar or polymerization to coke. PARTINGTON and SIDEBOTTOM (1959) showed by thermogravimetric measurements at atmospheric and reduced pressure that the char yield depended on the pressure, and they advanced a similar hypothesis. VAN KREVELEN *et al.* (1956) observed that when a coking coal was preheated at about 450°C and the residue subjected to a standard volatile matter content determination, the total volatile loss was

less than the volatile matter content of the coal. They explained their results on the assumption that in a volatile matter determination the rate of gas evolution was sufficiently high to remove some metaplast as a fog from the coal.

The present results show that a similar effect occurs in the two-stage carbonization of a high-volatile coal, and they prove that the increased yield of char is accompanied by a decrease in the tar yield. The most probable explanation of this observation is similar to that advanced by VAN KREVELEN. It is assumed that for a high-volatile coal, the volatilization of some primary pyrolysis products is markedly assisted by the evolution of gas, but that if these products are allowed to remain in the carbonized coal, further heating converts them to char. As shown in Table 2, the amount of gas evolved at 425°C is only about one-third of that evolved between 425° and 550°C. Consequently when the coal is carbonized to 425°C, the volatilization of the intermediate pyrolysis products is assisted by gas evolution to a smaller extent than at higher temperatures. The alternative reaction—the polymerization or condensation of the intermediate products to char—can therefore proceed at the lower temperature before the second stage of the carbonization is carried out.

The slow rate of heating in the Gray–King assay tends to reduce the difference between a direct and a two-stage carbonization since, even in the direct carbonization, the temperature of the coal is raised slowly through the important temperature range about 425°C. The tar yield from the direct carbonization will thus not be the maximum obtainable by isothermal carbonization at 550°C. This has been verified by means of carbonization in a fluidized bed, where the operating temperature was rapidly attained. The tar yields obtained in the first and second stage fluidized carbonizations were 6·4 per cent and 1·8 per cent respectively, which are similar to the corresponding yields obtained in the Gray–King assay. On the other hand, the tar yield obtained in the direct fluidized carbonization at 550°C was 12·8 per cent, which is significantly higher than the yield of 9·8 per cent in the Gray–King carbonization to 550°C. Thus the difference in yield between direct and two-stage carbonizations is more marked in fluidized carbonization than in the Gray–King carbonization where the heating rate is much smaller.

4. CONCLUSIONS

Under the conditions of combustion used in this investigation, the smoke emitted by coals and chars consisted almost entirely of unburnt tarry material. The amount of smoke emitted was determined by the total amount of tar evolved, and not by any particular constituent of the tar which might be preferentially removed by low-temperature carbonization. The chars emitted less smoke than coals of similar volatile content because of their lower tar content.

The low tar content of a smokeless char is mainly due to the removal of tar from the parent coal during the low-temperature carbonization. There is however another factor involved: some of the primary degradation products held in the decomposing coal during the preparation of the smokeless char undergo a polymerization or condensation reaction. As a result of this reaction, these primary products are not driven off at higher temperatures when the smokeless char is burned, and so do not contribute to the tar and smoke yield as they would if the coal itself were burned.

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VO
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1958

programme of the Scientific Department of the National Coal Board, and this paper is published with the permission of the Board.

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VOL.
1
958/9

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THE APPLICATION OF AN AIR POLLUTION CLIMATOLOGY TO TOWN PLANNING

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(*Received* 29 *December* 1958)

Abstract—In order to minimize urban air pollution problems, it is desirable to include meteorological evaluation in site selection for future industrial development. The complexity of the problem is emphasized, including such non-meteorological factors as population density, permissible threshold concentrations of pollution in relation to length and frequency of exposure, etc.

Brief descriptions are given of the seven ways in which emissions from elevated sources can cause high ground-level concentrations or depositions: gravity fall-out, orographic effects, the classical inversion situation, fumigations, downwash, the looping plume, and precipitation rain-out and wash-out. A reasonable problem is presented: to select from several possible industrial development sites the one that will minimize future pollution problems. It is shown that a theoretical solution, using Sutton's diffusion equations, requires simplifying assumptions and a very complete specification of the microclimatology of the city. The field determination of the parameters would be difficult and costly.

Wind direction frequencies under different meteorological conditions are given for the Windsor–Detroit area. These illustrate in a general way the type of variation to be expected under different stability, wind speed, and precipitation regimes in the absence of orographic and lakeshore effects.

Finally, it is suggested that if one is prepared to accept the frequency and strength of the morning fumigation as the criterion for air zoning, then it is possible to give a crude operational decision for town planning.

VO
1
1958

1. INTRODUCTION

AIR pollution control is practised in most large cities today. By introducing more efficient methods of combustion or suitable stack-cleaning equipment, it has often been possible to reduce pollution levels, even under pressure of expanding industrial development. The most notable example is in Pittsburgh (DEPARTMENT OF PUBLIC HEALTH, 1953) where the number of hours of heavy smoke diminished from 298 in 1946 to 16 in 1953. The observations were taken by the United States Weather Bureau from the top of a tall building in the down-town part of the city.

Although it is theoretically possible to scrub out nearly all obnoxious gases and particulates from a stack, there is an economic limit to the process. Recovery and disposal of the last 10 per cent of waste products can be very costly. Civic authorities do not wish local pollution ordinances to be so severe that industry is driven out of the area; in fact, many communities are attempting to attract new industry. A balance must therefore be found between added manufacturing costs and tolerable health, aesthetic, corrosion, and nuisance levels of pollution.

Within these terms of reference, then, cities are turning to town planning through the use of zoning by-laws. This generally has the support of industry, as well as the public, because it offers protection to the industrialist from the encroachment of residential areas. When a manufacturer locates in the country, a housing and

shopping development soon appears near his plant, forcing eventually some form of pollution control.

Unfortunately, the atmosphere cannot be regulated in the same way as can a blighted slum area. Under certain meteorological conditions a plume of smoke will travel for many miles with little dilution. It follows that a city cannot be divided into neat little compartments with respect to air pollution. Professional meteorological assistance is evidently required to select those areas that will minimize future pollution problems. This paper will be concerned with what shall be defined as " design criteria for air zoning ". Does there exist a rational meteorological basis for making an operational decision on site selection?

There are, of course, other sources of pollution such as automobiles and household incinerators. However, town planning is concerned primarily with the location of industrial emissions; the following discussion will be limited to that type of pollution.

2. THE AIR ZONING PARAMETERS

In order to reach the best air zoning decision, a number of factors must be considered.

(a) The air pollution climatology of the area should be known. Prevailing wind is an appealing concept that has sometimes been used. However, it is not at all obvious to the meteorologist that this will lead to the correct decision. The problem will be considered in detail later.

(b) The allowable threshold concentrations of various gases and particulates should be known. What percentage of the time is a given concentration permissible? Medical authorities do not yet agree on the effects of long exposures to the relatively low concentrations that usually occur in urban atmospheres. However, they do agree on the harmful effects of extreme smog " incidents " such as occurred at London (Royal Meteorological Society, 1954) and at Donora (Division of Industrial Hygiene, 1949). In this connection, it must be known whether the same standards are to be applied to all parts of the city. Is the object of town planning to protect property values in residential areas or to protect the health of occupants of blighted tenements? The meteorologist must know where the emphasis is to be placed before he can prepare design criteria.

(c) A related problem is the population density distribution. In the case of site selection for nuclear power plants, this is often integrated into the analysis, based on the premise that ground level concentrations should be weighted according to the average number of people at different points down-wind. The population is either counted or else a theoretical distribution is assumed. For example, an Atomic Energy Commission study (1957) of an imaginary city uses the function,

$$P = 200R^{2.83}$$

where P is the number of persons within a radius R in miles of the centre of the city. Beyond the city limits, a uniform population of 500 people per square mile is assumed.

Another special problem associated with nuclear power plants is radioactive decay rates; ground-level concentrations are a function of time as well as of the usual meteorological parameters. A review of the special methods of analysis that have been developed in the United States is given by Munn (1957). The present discussion will be limited to conventional forms of pollution.

VOL.
1
958/9

(d) The existing pattern of ground-level concentrations throughout the city should be known. The influence of new sources of emission can then be evaluated in relation to the present pattern. FRENKIEL (1956), assuming no change in efficiency of abatement methods and assuming an orderly growth of industry and population in Los Angeles County, has predicted mean hourly concentrations for the year 1980 at a particular sampling point. His approach merits careful consideration by city planners.

(e) The land available for industrial development is usually restricted by such factors as water supply, rail service, topography, the cost of real estate, etc. Air zoning is only one factor in town planning of land utilization. Hence, it will be weighted with other considerations, and the meteorologist may be asked to evaluate one site in comparison to another. This, perhaps, is a simpler question than that posed by FRENKIEL (1956) because the answer does not involve a quantitative calculation of pollution levels but only a relative comparison of two sites.

Before commencing work on a meteorological study, it is necessary to define carefully the problem to be solved. The preceding discussion has made it clear that the initial step is a very difficult task in the case of air zoning. Permissible threshold concentrations (in relation to length and frequency of exposure) have not been clearly defined by medical authorities. The present pattern of pollution is probably not known very accurately. Finally, the type of new industry and the strength of its emissions cannot be specified.

Under the circumstances, further discussions will be restricted to a consideration of the following. A town planning board wishes to reserve a large block of land for industrial development. Three or four sites meet all other requirements and a choice is to be made on the basis of minimizing future air pollution hazards or nuisances. This seems like a reasonable problem to bring to a meteorologist, although it presents many difficulties.

VOL
1
1958

3. THE METEOROLOGICAL FACTORS

A plume of pollution from an elevated stack first reaches buoyant equilibrium with its environment at some " effective " stack height. The plume is then transported downwind and is diluted by eddy diffusion. The diffusion process is often successful in preventing high ground-level concentrations of pollution. However, there are seven mechanisms that can produce unduly high surface concentrations or depositions.

(a) Gravity fall-out of large particles such as fly-ash. Modern industrial plants can successfully eliminate this nuisance at moderate cost through stack-cleaning equipment. It is therefore not regarded as a significant factor in site selection.

(b) Orographic intersection of the plume with higher terrain. If there is any choice at all, one should not locate new industry in a valley, particularly if there are residential areas on the sides of the valley. However, if such a site is necessary, local building ordinances should be designed so that stack heights and exit velocities and temperatures ensure effective stack height above the height of land.

(c) The classical inversion situation. Under such conditions, and over level terrain, the lateral spreading of a plume is within an angle of about 5° but the vertical diffusion is extremely small. The pollution is effectively " trapped " but it must be remembered that it is as difficult for the plume to spread down to ground level as it is for it to escape aloft. The inversion must therefore exist for a number of hours and

be accompanied by rather light winds. The historical pollution disasters were associated with inversions lasting several days.

(d) The fumigation situation (inversion aloft with lapse conditions below). The phenomenon was first described by HEWSON (1945). It may occur during the morning break-up of a radiation inversion or continuously along a coastline when an advection inversion disappears as air moves from over cool water to heated land. LOWRY (1951) has observed fumigation concentrations twenty times the strength predicted by SUTTON's diffusion model. It follows that coastline sites must be treated with suspicion in the absence of precise micrometeorological measurements.

(e) Aerodynamic downwash in the wake of the building. When strong winds are blowing, a turbulent vortex may form, causing the plume to curl down the side of the building. The effect is usually restricted to the plant property and can best be solved in the wind tunnel. Through the use of scale models, a certain orientation, shape of buildings, and stack height can be found that will minimize downwash. Except in combination with unusual orographic features, the effect is not regarded as significant in town planning.

(f) The looping plume. Under lapse conditions and with brisk winds, a turbulent eddy enclosing a puff of smoke can be brought down rapidly to ground level with little dilution of the pollution. This results in spasmodic bursts of high concentrations, each of which is of short duration. Increasing the height of the stack reduces the frequency of puffs but widens the area of influence. MUNN and KATZ (1958) have isolated the looping plume effect at a sampling station 5/6 mile from an elevated point source. It occurs under lapse conditions when the wind speed exceeds 11 knots.

VOL. 1 58/9

Another type of looping occurs when a plume acquires negative buoyancy due to cooling by the evaporation of water droplets. This is important, for example, in a wet flue gas-washing process; even during inversions, a moist plume may sink to the ground. The mechanism has been described by SCORER (1959) and he notes that it has not been considered in any published computations of down-wind concentrations. In the area of interest in the present paper, Detroit–Windsor, wet washing of flue gases is not practised to any significant extent, if at all. Hence, this type of looping will be neglected.

(g) Rain-out and wash-out by precipitation. Although it has been established that rain is a natural cleanser of the atmosphere, exact quantitative relationships are not known. Correlations at Leicester (DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH, 1945) indicate that up to 40 per cent of dissolved matter and up to 20 per cent of insoluble matter is brought down by rain. Theoretical treatments given by CHAMBERLAIN (1953) and others require too many simplifying assumptions. One of the complications is that wash-out is not uniform. A brief shower at the beginning of a period of continuous rain might be of over-riding importance. Presumably precipitation cannot be included in quantitative design criteria, although it would be of some interest to compare wind roses under precipitation conditions with conventional wind roses.

4. A THEORETICAL BASIS FOR METEOROLOGICAL DESIGN CRITERIA

The problem is to choose from amongst several tracts of land for industrial development. A theoretical approach can only be made with simplified assumptions.

(a) Assume an elevated point source at the centre of each tract of land.

(b) Assume the point source at some reasonable height, say 100 m.

(c) The emission strength may remain unknown but is presumed similar at the several sites.

If the microclimatology of the city is sufficiently well known, it is perhaps possible to calculate ground-level concentrations on a relative basis at various centre-line distances downwind under different stability conditions through the use of diffusion equations.

The classical Fickian approach to diffusion has not been successful for point sources because no theoretical expression has been found for the cross-wind transfer coefficient. SUTTON (1947) therefore proposed a statistical model, using dimensional reasoning and an appeal to mixing length theory.

If Q is the source strength and E the ground-level concentration at centre-line x downwind,

(a) under inversion conditions, (SUTTON, 1953)

$$E = \frac{2Q}{\pi C^2 \bar{u} x^{2-n}} \exp\left(\frac{-h^2}{C^2 x^{2-n}}\right)$$

(b) under lapse conditions, (SUTTON, 1953)

$$E = \frac{2Q}{\pi C_y C_z \bar{u} x^{2-n}} \exp\left(\frac{-h^2}{C_z^2 x^{2-n}}\right)$$

(c) under looping conditions, (HOLLAND, 1955)

$$E = \frac{2Q}{\pi C_y C_z \bar{u} (x^2 + h^2)^{(2-n)/2}}$$

(d) under fumigation conditions, (HOLLAND, 1955)

$$E = \frac{Q}{\pi^{1/2} C_y \bar{u} H x^{(2-n)/2}}$$

where $\bar{u}$ is the mean wind speed, h is the effective stack height, H is the height of the inversion, C, C_y, and C_z are generalized diffusion coefficients, and n is a stability parameter.

A three-dimensional Gaussian distribution of concentrations is assumed, the three variances being referred to the Lagrangian frame of reference. The stability parameter n is based on a power law wind profile. The diffusion coefficients depend on the mean wind, the gustiness n and the macroviscosity.

The model is essentially empirical and the parameters for each site must be determined by field testing. In practice, it is difficult to obtain values for the diffusion coefficients directly from meteorological measurements. The usual procedure, therefore, is to artificially release a plume, observe the downwind and crosswind concentrations, and indirectly calculate the diffusion coefficients from SUTTON's equations. Since the plume remains aloft under inversion conditions, there are very few such published values for elevated sources; there is in fact doubt about the equivalence of C_y and C_z in a stable atmosphere.

It is also to be noted that most of the published values of the parameters are for level terrain within 2 miles of a source. Nevertheless, some extensions have been made to greater distances and indicate that the Gaussian model provides a satisfactory approximation. For example, Tennessee Valley Authority data for distances of 50

VOL 1 1958/

miles have been used in an ATOMIC ENERGY COMMISSION study (1957). Another application on a similar scale is given by LUCAS (1958). However, for any particular urban area, the field determination of the parameters could be difficult and costly. In addition, in order to obtain annual frequency distributions of ground-level concentrations, it would be necessary to develop a rather extensive local microclimatology.

5. WIND DIRECTION FREQUENCIES UNDER VARIOUS METEOROLOGICAL CONDITIONS IN THE DETROIT–WINDSOR AREA

It is of some interest to examine the variations that do occur in prevailing winds under different stability, wind speed and precipitation conditions. These perhaps might provide an operational decision for two sites equidistant from the " centre " of a city. Tables 1 and 2 present some results from IBM tabulations prepared by the Climatological Division of the Canadian Department of Transport. A two year sample is represented. No attempt is made to define climatic modes; the tables merely illustrate variations within the sample.

TABLE 1. PERCENTAGE FREQUENCY OF WIND DIRECTION AT DETROIT CITY AIRPORT BY VARIOUS CLASSIFICATIONS OF LAPSE RATE FROM 20 TO 300 FT ABOVE GROUND AT DETROIT WJBK TV TOWER AND WIND SPEED

	N	NE	E	SE	S	SW	W	NW	C	Total no. of cases
0–4 knots										
Frequency of all cases	21	11	16	13	9	4	7	10	9	2184
Frequency of inversions and isothermals	22	11	13	11	10	5	7	9	11	1502
Frequency of large inversions*	21	11	9	11	8	4	9	15	13	539
5–9 knots										
Frequency of all cases	16	10	13	10	17	10	13	10		6776
Frequency of inversions and isothermals	17	9	9	1	21	13	18	13		2431
Frequency of large inversions*	13	12	3	8	12	14	22	14		318
10 knots or greater										
Frequency of all cases	13	7	4	3	12	20	25	16		6291
Frequency of inversions and isothermals	7	3	3	4	15	26	27	14		976
Frequency of large inversions*	insufficient cases to provide a representative sample									17
Frequency of lapse cases	14	7	5	3	11	19	24	16		5315
Totals										
Frequency of all cases	15	9	10	8	14	13	17	13	1	15,251
Frequency of inversions and isothermals	17	8	9	5	16	13	17	12	3	4909
Frequency of large inversions*	18	11	7	10	10	8	14	15	8	874

* Inversions greater than 5°F.

The Detroit–Windsor area is characterized by flat terrain with no special orographic effects. There is some evidence for a land–lake circulation in the spring and early summer from both Erie and St. Clair but the effect is not at all sharp. There is also evidence of a city " heat-island " effect; during periods of light gradients and clear skies, the city generates its own city–country circulation. Studies by BAYNTON and WHITE (1958) have indicated that for winds less than 5 miles/hr there can be wide

variations throughout the metropolitan area; in fact it is probably impossible to define an areal wind direction under light gradients. For stronger winds and for locations away from the lakes, there is good agreement at different observing sites for the class limits established in this study. Hourly Detroit City Airport winds are used because that site is closer than any other to the heart of the City. For no special reason, precipitation records have been chosen from the same observing point.

Hourly vertical temperature differences were obtained from WJBK TV Tower, located 10 miles to the northwest of down-town Detroit in flat grassy country. In this study only the 20–300 ft temperature values are used. The effect of spatial variations in lapse rate throughout the area have been reduced to a minimum because the lowest temperature level is 20 ft above the ground, thus smoothing out some of the variations, and because only three broad classes of temperature differences have been tabulated. In this connection it is noted that the isothermal rather than the adiabatic has been used as a class limit. Although the adiabatic is critical for thermal turbulence, mechanical turbulence can still occur under weak lapse and inversion conditions. It is convenient, and is becoming customary, to arbitrarily select the isothermal as the limit for significant mechanical turbulence, although admittedly it would be more logical to adopt a sliding scale relating both temperature difference and wind speed.

Table 1 shows the variations of wind direction frequencies in different stability and wind speed classes. As previously noted, the class 0–4 knots is not representative of the area and is included merely to complete the display of cases. The prevailing wind for the total two-year sample is westerly and it is seen that this is generally true also in the various sub-classes. However, there is some variation in the percentages, i.e. the relative advantage to be gained in choosing one direction to another.

The looping plume occurs under lapse conditions with winds of 10 knots or over. By choosing a site in the eastern quadrant of the metropolitan area, the effect can be almost eliminated for the main population density. If it be assumed that undesirably high ground-level concentrations occur downwind about 30 per cent of the time that a looping plume is blowing, then such conditions will occur to the west of a stack only about

$$\left(\frac{30}{100} \times \frac{5}{100} \times \frac{5315}{15251}\right)$$

or 0·5 per cent of the total time. At a similar distance to the east of the factory, the percentage will be fivefold.

Table 1 requires careful interpretation under inversion conditions. Gaseous pollution from elevated sources in the Detroit–Windsor area does not diffuse down to ground-level in particularly high concentrations during an inversion. This is presumably because there have been no instances in the period of record of a low-level inversion persisting for several days. (At a lakeshore location at Monroe, Michigan, on the other hand, a continuous 60 hr advection inversion has been observed.) The high gaseous concentrations at the Detroit–Windsor Sampling Stations usually come at the time of the morning break-up of the inversion—the fumigation.

With respect to suspended particulates, the classical build-up of pollution during inversion conditions is observed, the final surge occurring during the fumigation. This is attributed to the effect of gravity on particulates and to a lower average height of emission.

TABLE 2. PERCENTAGE FREQUENCY OF WIND DIRECTION AT DETROIT CITY AIRPORT UNDER SPECIFIED METEOROLOGICAL CONDITIONS

	N	NE	E	SE	S	SW	W	NW	C	Total no. of cases
Frequency of all cases	15	9	10	8	14	13	17	13	1	15,251
Frequency in 3-hr period following a morning fumigation	14	10	10	6	13	16	17	16	0	639
Frequency when precipitation of 0·01 in 1 hr or greater is falling	11	14	16	10	23	11	10	5	1	1013

For gaseous pollution, therefore, it is of some interest to look at wind direction frequencies during fumigations. This has been done subjectively in Table 2. A tabulation has been made of wind directions in the 3-hr periods following the break-up of each nocturnal inversion. The time of day is variable because of the seasonal shift in the hour of sunrise and other factors. The wind during fumigations is not used because the associated eddy structure at that time makes the wind direction quite variable and unrepresentative. Questionable cases have been eliminated, and wherever possible the cycle of ground-level concentrations of sulphur dioxide has been used to confirm the fumigation.

It is believed that Table 2 gives a reliable sample estimate of the frequency of fumigation for different wind directions. Again the results are quite similar to conventional wind frequencies, although a chi-square test indicates significant differences at exactly the 95 per cent confidence level. For fixed distances from the centre of the city, one is again led to the conclusion that industrial development sites should be chosen in the eastern quadrant of the metropolitan area. (The weighting effect of distance will be discussed in Section 6.)

Table 2 also includes wind direction frequencies during precipitation. The pattern is quite different and shows a prevailing southerly wind. If rain-out and wash-out are made the criteria for air zoning, then new industry should be located in the north-west quadrant of the area. This is in conflict with previous conclusions and places the meteorologist in a dilemma. Since there is no suitable physical model for calculating depositions of pollution by precipitation, the working compromise would probably be made of eliminating from further consideration sites to the south of the metropolitan area and neglecting the effect of precipitation in all other directions.

The two tables, of course, do not give any indication of wind direction frequencies during extreme smog situations. There has been no experience during the period of record to define an air pollution climatology of extremes. VERYARD (1958) has examined for London, England, all occasions in the last forty years of fog comparable with that of the smog of December 1952. He found 12 such cases of which 8 were associated with a light easterly gradient around a continental anticyclone. (The prevailing wind is westerly.)

6. THE COMBINED EFFECT OF DISTANCE AND DIRECTION ON SITE SELECTION

Tables 1 and 2 illustrated the effect of direction on frequency of high concentrations. Suppose now, that sites A and B are in different directions and at different distances from the centre of the city. This is a much more realistic problem in town planning.

VOL. 1 58/9

It should be emphasized immediately that there is no simple relationship between ground-level concentrations and distance downwind from the emission. This may be seen from SUTTON's diffusion equations (see Section 4) in which the centre-line distance x occurs in the numerator in an exponential term and also in the denominator raised to the power $(2-n)$.

As noted previously, a theoretical solution requires a rather complete specification of the microclimatology of the city. In addition, under inversion conditions the diffusion coefficients are almost impossible to determine experimentally. However, the problem is simplified considerably if we are prepared to accept the morning fumigation as an inversion index for site selection (neglecting for the moment the looping plume).

HOLLAND (14) has modified SUTTON's equations for the special case of fumigations:

$$E = \frac{Q}{\pi^{1/2} C_y \bar{u} H x^{(2-n)/2}}$$

where the nomenclature is as given previously.

Let the centre, O, of the city be at distances x_1 and x_2 from proposed sites A and B respectively. Let the ground-level concentrations when O is downwind under fumigation conditions from A and B by E_1 and E_2 respectively. Let the relative frequency of fumigations with vector wind directions **AO** and **BO** be F_1 and F_2. Then an index for site selection will be the ratio,

$$\frac{F_1 E_1}{F_2 E_2} = \frac{F_1}{F_2}\left(\frac{x_2}{x_1}\right)^{(2-n)/2}$$

If the ratio is greater than one, choose site B; if less than one, choose A.

It is seen that all terms have cancelled with the exception of $x^{(2-n)/2}$. Values of the stability parameter n range from 0·2 with superadiabatic lapse rates to 0·5 with large inversions and are independent of the height of emission. Although n cannot be calculated without vertical profiles of wind and temperature, it will lie within the range 0·2 to 0·4 during morning fumigations. Hence the exponent will be in the range 0·9 to 0·8. In view of other assumptions inherent in the analysis, this is a satisfactory approximation.

The method may be illustrated by using the data in Table 2. Suppose it is required to compare a site 4 miles to the southeast of the metropolitan area with another 8 miles to the west.

Then,

$$\frac{F_1 E_1}{F_2 E_2} = \frac{10}{17}\left(\frac{8}{4}\right)^{0\cdot9 \text{ or } 0\cdot8}$$

For the exponent 0·9, the ratio is 1·11 and for the exponent 0·8 it is 1·02. In either case the site 8 miles to the west is slightly preferable to the one 4 miles to the southeast—on the basis of frequencies and relative strength of fumigations.

For the looping plume from an elevated source, HOLLAND (1955) suggests that the diffusion coefficient C_z must be extraordinarily large. Hence, for large x, the exponential term in SUTTON's anisotropic diffusion equation must approach unity, the equation reducing to,

$$E = \frac{2Q}{\pi C_y C_z \bar{u}(x^2 + h^2)^{(2-n)/2}}.$$

VOL 1 1958

If F_1 and F_2 are the relative frequencies of looping plume concentrations E_1 and E_2 in the directions **AO** and **BO** respectively, then the required ratio reduces to

$$\frac{F_1E_1}{F_2E_2} = \left(\frac{x_2^2+h^2}{x_1^2+h^2}\right)^{(2-n)/2}$$

However, the analysis is questionable because C_z depends upon surface roughness elements, amongst other things. Hence, there are likely to be significant variations throughout a city and the term should not properly be cancelled from the ratio. For example, a standard reference on diffusion theory (ATOMIC ENERGY COMMISSION, 1955) states that looping plumes are most common during light winds whereas MUNN and KATZ (1958) have found a required minimum speed of 11 knots at a Windsor sampling situation. The large roughness elements of city buildings no doubt account for the difference.

It is of interest to compare the relative order of magnitude of ground-level concentrations, E_F and E_L, under fumigation and looping conditions respectively.

$$\frac{F_FE_F}{F_LE_L} = \frac{F_FQ}{\pi^{1/2}C_{y_F}\bar{u}_FHx^{(2-n_F)/2}} \Big/ \frac{F_L2Q}{\pi C_{y_L}C_z\bar{u}_L(x^2+h^2)^{(2-n_L)/2}}$$

$$= \frac{F_F2\pi^{1/2}}{F_L}\frac{\bar{u}_L}{\bar{u}_F}\frac{C_z}{H}\frac{C_{y_L}}{C_{y_F}}\frac{(x^2+h^2)^{(2-n_L)/2}}{x^{(2-n_F)/2}}$$

Assume $\bar{u}_L = 3\bar{u}_F$, $C_{y_L} = C_{y_F}$, $n_L = n_F = 0{\cdot}2$.

In the Detroit–Windsor area $F_F/F_L \cong 0{\cdot}15$ assuming that a fumigation lasts $\frac{1}{2}$ hr and that there are high ground-level concentrations 30 per cent of the time that a looping plume is blowing.

Then the ratio has the order of magnitude of $\frac{1{\cdot}5C_z}{H}\left(\frac{x^2+h^2}{x}\right)^{0{\cdot}9}$. For distances of 2 miles or greater h can be ignored. H is of the order of magnitude of 800 ft. Very little can be said about C_z except that it is at least 0·2 (see for example the Harwell data, STEWART *et al.*, 1958) and is probably greater than 1 during looping. The ratio is therefore within or greater than the following range of values:

TABLE 3

	C_z	
Distance downwind	0·2	1·0
2 miles	1·6	7·8
3 miles	2·3	11·3

Certainly, then, for distances much greater than 2 miles, the fumigation is more important than the looping plume. Intuitively, this seems natural because the decrease of concentrations with downwind distance during a fumigation depends upon the slight lateral spread of pollution during the preceding night. A looping plume, on the other hand, is under the influence of the entire eddy spectrum of lapse conditions with no inhibiting upper inversion. Two miles is therefore a rather liberal estimate of the distance downwind in which an individual eddy containing high gas concentration can maintain any semblance of its identity under lapse conditions. It

VOL. 1 58/9

follows that in cases where the range of interest in air zoning lies in distances of more than 2 miles, the looping plume effect may be ignored.

7. CONCLUSION

This paper has emphasized the complexity of meteorological evaluation in town planning. Without an extensive knowledge of the microclimatology of a city, and without simplifying assumptions, it is not possible to give a theoretical solution to the problem. In addition, the effect of the precipitation mechanism must be ignored or considered subjectively.

If lapse rate data are available for one representative site in the city and if there are no large disturbing orographic effects, then a method is presented for making a crude operational decision for certain town-planning problems. This is based on the frequency and strength of morning fumigations. However, the method cannot be applied when considering distances of less than 2 miles from proposed industrial sites. In addition, the extreme situation in which an inversion lasts several days has been ignored because there has been no experience in the Detroit–Windsor area to define the relationships.

It is hoped that this paper will stimulate interest in the difficult meteorological problem of air zoning.

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VOL.
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958/9

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THE AVERAGE SIZE OF SUBMICRON PARTICLES

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Abstract—The best criterion of the efficiency of air cleaning is the number of submicron particles remaining in the cleaned air. When a volume is to be maintained at a high level of cleanliness, it is not enough to filter particulates from the incoming air. The air may contain gases which can react later to produce particles within the volume or particles may be created by some activity within the volume.

The *number* of particles in the air may be measured at any time with a photoelectric nucleus counter. The mass per particle counted may vary by a factor of 10^6 or more and therefore a size spectrum is most desirable in evaluating the amount of contamination or in tracing the source of contamination. Particles resulting from gas reactions are usually in the 10 to 50 Å range of radii whereas leakage of unfiltered air produces particles in the neighborhood of 300 Å.

A size spectrum is somewhat of a chore to obtain, but an average size can be obtained easily. The charge distribution on a population of particles follows Boltzmann's law and it is shown that an average size may be obtained by measuring the total number of particles and the number of uncharged particles. The uncharged particles are obtained by passing the aerosol through an electric field which is intense enough to pull all the charged particles out of the air stream. The relations between size of particle and the charge distribution are given in graphical form. The auxiliary apparatus needed for the determination of average size is shown.

VO
1
1958

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IN most urban or suburban localities, combustion produces the majority of airborne particles. The most numerous size usually runs around 3×10^{-6} cm radius, and substantially all of them will be within a 10 to 1 range of radii. On the small end of the spectrum coagulation is more rapid and the little ones combine with one another or build up some of the larger ones. At the large end of the spectrum gravity starts to have an effect and fall-out occurs.

Aerosols are a mixture of sizes and no one number can describe the mixture. There can be many kinds of averages—average radius, average surface, average mass, etc. Another type of average size can be given as an equivalent monodisperse (single-sized) aerosol. For example, we can measure the uncharged fraction in an unknown aerosol and say that its " average " size is that of a monodisperse aerosol which would have the same uncharged fraction of particles. Other properties could be used for comparison such as diffusion, supersaturation required to cause condensation, or coagulation rate. These average sizes will not agree with one another very well if the spread in size is large. Nevertheless, the simple concept of an average size is useful as long as the limitations are remembered. At the present stage of the technology the comparative simplicity of measuring the uncharged fraction of an aerosol makes it possible to get a size parameter which, with all its limitations, is better than none. The first requirement is that the aerosol be in electrical equilibrium. Newly born particles may not have reached equilibrium but this can be remedied by an exposure to radiation by an X-ray machine or a small radioactive source. A polonium

source, of the type used as " static eliminators " on phonograph records will do the job if sealed in the sampling line. The time to reach equilibrium is decreased as the intensity of radiation is increased but the final fraction of uncharged particles is not affected. Intense radiation can produce nuclei under some conditions and while this should be guarded against it will rarely be a problem.

CHARGING MECHANISM

A monodisperse aerosol becomes charged in natural conditions due to the presence of " small ions " which are produced by cosmic rays and natural or man-made radioactivity. The birth rate of small ions over the ocean is about 2 positive and 2 negative ions per cm^3 per sec. Over the land the value is about 10 ion pair per cm^3 per sec. These small ions collide with themselves and with the larger aerosol particles. When a positive and negative small ion come together a pair of ions is lost. When a small ion hits a neutral particle, a charged particle is produced and a small ion and a neutral particle are lost. When a small ion hits a particle already singly charged with the opposite sign a neutral particle is produced and a small ion and a charged particle are lost.

This continuous interchange of charge on particles and loss of small ions can be calculated if the combination coefficients are known. This has been done with varying results. Another approach was reported by P. J. NOLAN (1956) and credited by him to Dr. E. F. Fahy which applies the Boltzmann law to the distribution of charges.

$$\frac{N_0}{N_p} = \exp\left[\frac{p^2e^2}{2rKT}\right] \cong \exp\left[\frac{2{\cdot}8p^2 \times 10^{-6}}{r}\right] \tag{1}$$

where p = number of electronic charges
e = electronic charge
r = radius of particle
K = Boltzmann's constant
T = degrees Kelvin
N_0 = uncharged nuclei
N_p = nuclei of p charges.

The term $\frac{p^2e^2}{2r}$ is the energy due to p electronic charges on a sphere of radius r. The value of p goes through values of $+1$, -1, $+2$, -2, etc. If Z = the total number of particles per cm^3,

$$Z = N_0 + 2N_0 \exp\left[\frac{-2{\cdot}8 \times 10^{-6}}{r}\right] + 2N_0 \exp\left[\frac{-4 \times 2{\cdot}8 \times 10^{-6}}{r}\right] + 2N_0 \exp\left[\frac{-9 \times 2{\cdot}8 \times 10^{-6}}{r}\right]. \tag{2}$$

If we let $\exp\left[\frac{-2{\cdot}8 \times 10^{-6}}{r}\right] = X$,

$$Z = N_0 + 2N_0X + 2N_0X^4 + 2N_0X^9 + \ldots + 2N_0X^{p^2} \tag{3}$$

where N_0 = uncharged particles and successive terms are for singly, doubly, triply, etc. charged particles of either sign.

When the radius of the particle is less than 5×10^{-6} cm the series converges rapidly and the uncharged fraction $F_0 = N_0/Z$ can be found from

$$F_0 = \frac{1}{1+2(X+X^4+X^9)} \quad (r < 5 \times 10^{-6}) \tag{4}$$

An alternative expression can be used to evaluate F_0 for larger radii

$$F_0 = \frac{1}{1{\cdot}06(r \times 10^6)^{\frac{1}{2}}} \quad (r > 5 \times 10^{-6}). \tag{5}$$

MOBILITY

A charged particle in an electric field will tend to move with the electrical forces and will be held back by air resistance. The effect of inertia is almost wholly negligible in the submicron sizes and the limiting velocity is attained in a very short distance. Mobility is defined as the velocity in cm/sec that a charged particle attains in a field of 1 volt/cm or, velocity

$$V = EM \tag{6}$$

where E is measured in volt/cm, V in cm/sec and M in cm/sec per volt/cm: Values of M for singly charged particles (F_0), and the fraction of total with single and multiple charges are given in Fig. 1. The mobility for p charges is equal to the singly charged mobility multiplied by p.

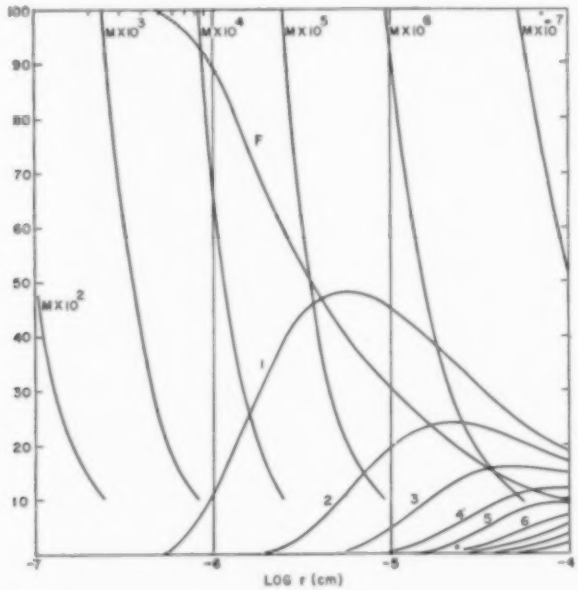

FIG. 1.—F = number of uncharged particles in per cent of total number of particles.
1, number of singly charged particles in per cent of total number of particles.
2, 3, etc. number of doubly-charged, triply-charged, etc. particles in per cent of total number of particles.
M = Mobility of singly charged particles in cm/sec per volt/cm.

The total number of particles can be measured with the photoelectric counter. The charged fraction can be removed by passing the aerosol through an electric field to remove the charged fraction and the uncharged fraction can then be measured. From the ratio of these readings and Fig. 1 an equivalent size can be obtained. The dimensions of the electric field and the voltage used are not critical as long as:

(1) The losses by diffusion in passing through the field are small, and
(2) All of the charged particles are removed.

The diffusion losses are negligible if a measurement of the particle count with the field structure or " denuder " in the sampling line (but not energized) is the same as a measurement without the denuder.

A typical denuder is shown in Fig. 2. The inner cylinder has an outer diameter of $\frac{5}{8}$ in., the outer cylinder an inner diameter of $1\frac{3}{8}$ in., and the straight portion is $5\frac{1}{2}$ in. The applied voltage should be between 5 and 10 kV. With a flow of 100 cm³/sec diffusion loss will not be excessive for small particles normally encountered, and it will remove substantially all of the charged particles in normal air.

The denuder is conveniently made of concentric cylinders with the inlet and outlet arranged to minimize turbulent flow. An approximation of the collection efficiency of the denuder can be obtained by assuming it to be the equivalent of a parallel plate combination of corresponding area, length and spacing.

A = area of annulus = bh
Q = flow, cm³/sec
h = spacing between plates
b = mean circumference
v = voltage across plates

$$\text{Longitudinal transit time} = \frac{lA}{Q}\ \text{sec} = \frac{lbh}{Q}$$

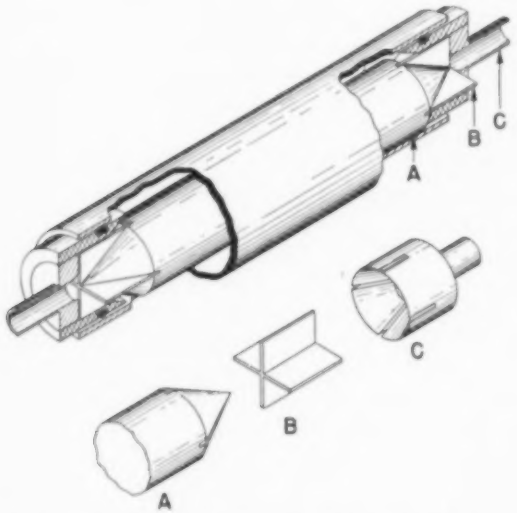

FIG. 2. Example of " denuder " used to remove charged particles from an aerosol.

Particle velocity $ME = \frac{Mv}{h}$ cm/sec

Transit time radial $= \frac{h^2}{Mv}$ sec (inner to outer cylinder or vice-versa) (7)

for a critical mobility at which all particles are caught

$$\frac{h^2}{M_c v} = \frac{lbh}{Q} \therefore M_c = \frac{Qh}{lbv}.$$

All charged particles with a mobility equal to or greater than M_c (Fig. 1) will be removed. Fig. 1 shows the proportion of multiply charged particles of a given size. For example, 20 per cent of the particles with a radius of 10^{-5} cm have two charges, and therefore a mobility twice that of the 45 per cent that are singly charged. If the denuder will collect all the singly charged particles it will collect all of the multiply charged particles. This information on multiply charged particles is not needed in finding an equivalent size, but is included to round out the picture.

Diffusion

To estimate diffusion loss as a fraction of original aerosol use

$$f_0 = \frac{S}{V}\sqrt{\left(\frac{M_1}{40}\, t\right)} \tag{8}$$

where S = surface in cm²
V = volume in cm³
M_1 = singly charged mobility
t = average dwell time in the volume
$t = V/Q$ (Q = flow, cm³/sec).

Equation 8 is used to see that there are only minor losses due to the smallest particles being studied; it is not a basic formula.

CONCLUSIONS

A method of obtaining an average size of submicroscopic particles is described which depends upon a determination of the fraction of particles which are uncharged. This can be done by a count of particles before and after passing the aerosol through a strong electric field. At present the only convenient means of doing this is the photo-electric nucleus counter and it has been used for this purpose for many years in various laboratories around the world. Complete equipment for industrial applications is not available commercially, but any capable experimentalist could make the accessories needed.

" Clean rooms " in industry are increasingly important and have become so free of airborne material that improvement or even maintenance requires monitoring the submicroscopic particles. A knowledge of average size can be a clue to the origin of the contamination. Leakage around filters or doors will usually show an uncharged fraction of 0·5 while a sparking contact or photo-chemical gas reactions produce nuclei with an uncharged fraction of 0·1 or less.

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VOL 1 1958

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Review Articles

COUNTING OF AITKEN NUCLEI AND APPLICATIONS OF THE COUNTING RESULTS

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(*Received* 22 *December* 1958)

Abstract—The paper deals with instruments for determining the concentration of condensation nuclei of approx. 10^{-5} to 10^{-7} cm radius and discusses the uses made of concentration measurements. The importance of condensation nucleus research for meteorology, medicine and industry is briefly mentioned.

The absolute condensation nucleus counters in which the nuclei converted into droplets are directly counted, are reviewed and the most recent and much improved types with photographic and stereophotomicrographic recording described. The efficiency of these counters, its dependence on the expansion ratio and the frequency distribution of counts are discussed.

A description of the only relative condensation nucleus counter which has now been developed to a very high degree of accuracy and dependability, is given. This counter measures by means of a photo-cell the extinction of a light beam traversing the fog formed by an adiabatic expansion. The accuracy and the improvements incorporated in the photo-electric nucleus counter Model 1957 together with some processes taking place in the fog of the cloud chamber of the instrument which affect the measurements, are discussed.

A survey of the following uses of the counting results is given: for climatological statistics of nucleus concentrations and their relationship to meteorological elements dealing not only with the concentration of nuclei but also with their size and charge-distribution; for special investigations with the aid of mobile photo-electric nucleus counters; droplet size of fog; disappearance of nuclei in a closed vessel; determination of the diffusion coefficient, size and mass of nuclei; air-conditioning equipment, control of air pollution in cities and development of improved electrical control devices.

VOL.
1
958/9

CONDENSATION nuclei are invisible, minute particles contained in the air in various quantities acting during the condensation process as cores for the water droplets which constitute artificially produced or natural clouds and fog. Their natural sources are volcanic eruptions, salt crystals from evaporated sea-spray drops, smoke of forest fires, etc.; nuclei are also produced by human activity e.g. by domestic and industrial combustion processes, exhaust from motor vehicles, jet aeroplanes, electrically heated wires (electric fires) and even from the glass envelope of electric bulbs. One puff of cigarette smoke contains hundreds of thousands of condensation nuclei per cm^3 of about 10^{-6} cm radius. On the other hand in the clean maritime air on the west coast of Ireland (POLLAK and MURPHY, 1952) or on the Greenland ice less than 100 nuclei per cm^3 have been measured.

The importance of the condensation nuclei for meteorology is best expressed by the memorable statement, still valid today, of the pioneer of condensation nucleus research JOHN AITKEN some 70 years ago that without nuclei there would be no fog, no cloud and probably no rain since the large supersaturation required for the formation of fog or cloud droplets without the assistance of condensation nuclei never takes place in our atmosphere.

Quite recently the importance of condensation nuclei for industrial purposes and their value in the treatment of certain diseases was discovered.

We will deal here only with condensation nuclei of sizes between approx. 10^{-5} and 10^{-7} cm radius which today are called Aitken nuclei. On account of their minute size they cannot be seen with any optical microscope and the use of an electron microscope which was successfully applied for studying the nature of the nuclei, is hardly feasible for counting. Fortunately, about 75 years ago a simple and ingenious method was devised so as to make the condensation nuclei visible and possible to count, namely by converting them into droplets and thus magnifying their size.

The formation of droplets around the condensation nuclei in a fixed volume of air saturated with water vapour can be achieved by producing supersaturation either by increasing the pressure in the vessel and suddenly releasing it (COULIER, 1875) or by expanding the volume by a predetermined amount using a pump for partial evacuation of the cloud chamber (AITKEN, 1880/81).

The number of droplets formed depends on the expansion ratio. FOITZIK (1950) experimenting with a large model of the Scholz nucleus counter at Lindenberg found that with supersaturations of 110 per cent (expansion ratio approx. 1·01) only 1/40 to 1/20 of those nuclei are converted into droplets which fall out with 300 per cent (expansion ratio about 1·19), and only 1/20 to 1/10 of those which are precipitated with 140 per cent supersaturation (expansion ratio approx. 1·05). We shall revert to these important results later.

1. COUNTING OF AITKEN NUCLEI

We distinguish between *absolute* and *relative* condensation nucleus counters. With the absolute counters the droplets into which the nuclei are converted by one of the two methods mentioned above, are precipitated on a graticule and counted directly by eye through a magnifying glass in dark-field illumination or on photomicrographic records. The relative counters measure by means of a photo-cell either the extinction of a light beam traversing the fog, formed by the expansion, or the intensity of the scattered light perpendicular to the beam. In the first case barrier photo-cells have proved adequate and very convenient, but in the latter photo-multipliers are required. Other properties of the fog, however, could be used for constructing relative condensation nucleus counters. The relative counters require calibration with reference to an absolute nucleus counter.

Absolute condensation nucleus counters

The following constitute the instruments so far constructed: The Portable Aitken Nucleus Counter (with a range up to 25,000 nuclei/cm³ if the pump is used for sampling), the Aitken–Lüdeling–Wigand Pocket Nucleus Counter (range 55 to 140,000 nuclei/cm³), the large model of the Scholz counter with an arrangement for measuring the number of charged nuclei (range 7 to 1,660,000 nuclei), the small Scholz counter (range 5 to 950,000 nuclei), the Pollak–Daly condensation nucleus counter with photographic or stereo-photomicrographic recording (range with *eye observations* 21 to 350,000 nuclei/cm³; upper limit of the range when the droplets are *photographed* at least 3 million nuclei/cm³).

For the descriptions of the older instruments and their operation we refer the reader to the surveys in English (up to roughly 1938) by LANDSBERG (1938) or MASON (1957) up to 1957 and the original publications (POLLAK, 1952 and POLLAK and DALY, 1957).

The many defects and limitations of the Portable and Pocket Aitken Nucleus Counters are thoroughly discussed in KLEINSCHMIDT's Handbuch (1935) although some more could be added. The main source of trouble, according to all users of the Pocket Counter, is leakage. By submerging the counter in water and pumping-in air, leakages are easy to detect but sometimes difficult to remove. The Scholz counters represent a marked improvement, particularly on account of the reduced turbulence in the receiver, although they also are not leak-proof and the counting difficulties are as great as in the Portable and Pocket Counters. Common to all these counters is the necessity to combine at least ten and, according to English practice, twenty single observations—taking together with the counting of the second and third showers about 15 to 30 min—so as to give an average in order to increase the accuracy of the measurement. Even so, the accuracy of the measurements with these counters is, at best, 10 per cent and in many cases only 20 per cent.

The older counters use for counting the droplets precipitated on the stage simple lenses of low magnification, so that droplets below a certain, by no means negligible size escape counting.

The Pollak–Daly* absolute counters were constructed for special field work and for re-calibrating the relative photo-electric nucleus counter which was long overdue on account of its development over the last ten years and of its now world-wide use. Since these counters use vacuum taps and microscope with photographic equipment they are not pocket instruments. The micrographic equipment, however, can be easily detached and separately packed, so that these counters are quite portable instruments.

The Pollak–Daly counter with photographic recording (POLLAK, 1952) permits simultaneous observations of the graticule by two persons or the observations of the graticule by one person and the synchronous photographic recording of the droplets on 35 mm film strip, single plates (6·5 × 9 cm) or roll film (6 × 9 cm) on which sixteen exposures can be taken. With one exposure, the droplets on 24 squares of the millimetre graticule can be recorded so that a repetition of the necessary operations required by other counters in order to obtain an average count becomes superfluous and the time taken for one experiment is reduced to ¾ min. The limitation to 5 droplets/mm² recommended hitherto for all existing nucleus counters used for eye observations is removed when the droplets and the graticule are photographed. By using a special sealing arrangement (0–rings) and employing vacuum taps, leakages are practically impossible and were never observed. The glass windows of the receiver are interchangeable with plates of conducting glass which can be heated by the passage of an electric current. The construction ensures that the 1 cm distance above the graticule is always maintained, independent of the tightening of the sealing arrangement. In order to utilize the advantages of photographic recording more fully, a movable graticule has been built-in. A lever arrangement enables exposing unused parts of the graticule in quick succession without the necessity of waiting until the droplets of each shower have evaporated. The counts of the 2nd, 3rd, etc. showers (" Nachzügler ") have to be added to the number of droplets counted at the first expansion. Their omission constitutes a serious error in concentration measurements.

The previous illumination of the graticule by a light source and mirror, the centre

* Mr. J. DALY is Chief Mechanic in the School of Cosmic Physics and was, on an overtime basis, my collaborator until 31 October 1958.

VOL. 1 58/9

of which was blackened out, has been replaced by a perfect dark-field illumination using an electric bulb which ensures constant illumination indispensable for uniform exposures of microphotograms.

The receiver is equipped with a stirrer operated from outside by a permanent magnet. Two easily detached pumps are provided; one for purifying the air in the receiver and for the dilatation, the other for sucking the sample of impure air into the receiver.

The counter with stereo-photomicrographic recording (POLLAK and DALY, 1957) permits better discrimination in photograms of the graticule, between droplets formed around the nuclei and spurious condensation products or extraneous matter on both sides of the graticule. Stereo-photographic recording makes it possible to dispense with the glass graticule altogether and to follow the tracks of the droplets during their fall in the receiver. Their counting in any plane or volume is carried out by methods as used in stereo-photogrammetry. The most recent model with reduced turbulence in the receiver and several other improvements is described by POLLAK and DALY (1958) and shown in Fig. 1.

The minimum size of the droplets which can be seen or photographed by the present arrangement in the counter with photomicrographic recording is about 0·001 in. (=0·025 mm). There is, however, no difficulty in increasing the resolving power of the microscope used.

The efficiency of the Aitken-type nucleus counters has quite often been discussed (HOSLER, 1950; HOSLER *et al*, 1952; OHTA, 1955). We have to distinguish between the loss of nuclei by deposition and diffusion when entering the receiver and that by decay processes in the chamber after the air sample has been enclosed. The first mentioned losses can be reduced by using taps with wide bores. The losses in the receiver due to time lapse between sampling and expansion may be due to coagulation, diffusion and sedimentation. Other losses may be attributed to the fact that condensation does not take place on some of the nuclei and they escape subsequent expansions; or to droplets formed after expansion on the nuclei evaporating before they reach the counting stage. Droplets under a certain size cannot be detected even though they may have fallen on the stage. Thus, the efficiency of the counter depends also on the resolving power of the optical system used.

Simple calculation shows that the losses due to coagulation are negligible. Gravitational sedimentation affects the large nuclei which fall rapidly on the stage of the counter before expansion is made. These large nuclei missed in the counts are of particular importance for meteorological problems. The diffusion effect as an explanation of the deficiency of the number of nuclei detected in the Aitken counter as compared with the concentration determined by an electron microscope was studied theoretically by OHTA (1955). He shows that in a cylindrical receiver of 1·0 cm height and 3 cm diameter the number of nuclei having diameters smaller than 2×10^{-6} cm will be reduced to 89 per cent or less in the time lapse of 10 sec, and to 79 per cent or less in 30 sec.

Last but not least, the efficiency of a counter depends on the expansion ratio applied. This last effect already mentioned but given far too little attention up to now, is most strikingly shown in Table 1.

With an expansion ratio of 1·02 (supersaturation 110 per cent) only about 310 nuclei were found, which is in good agreement with the number of droplets generally

VOL.
1
58/9

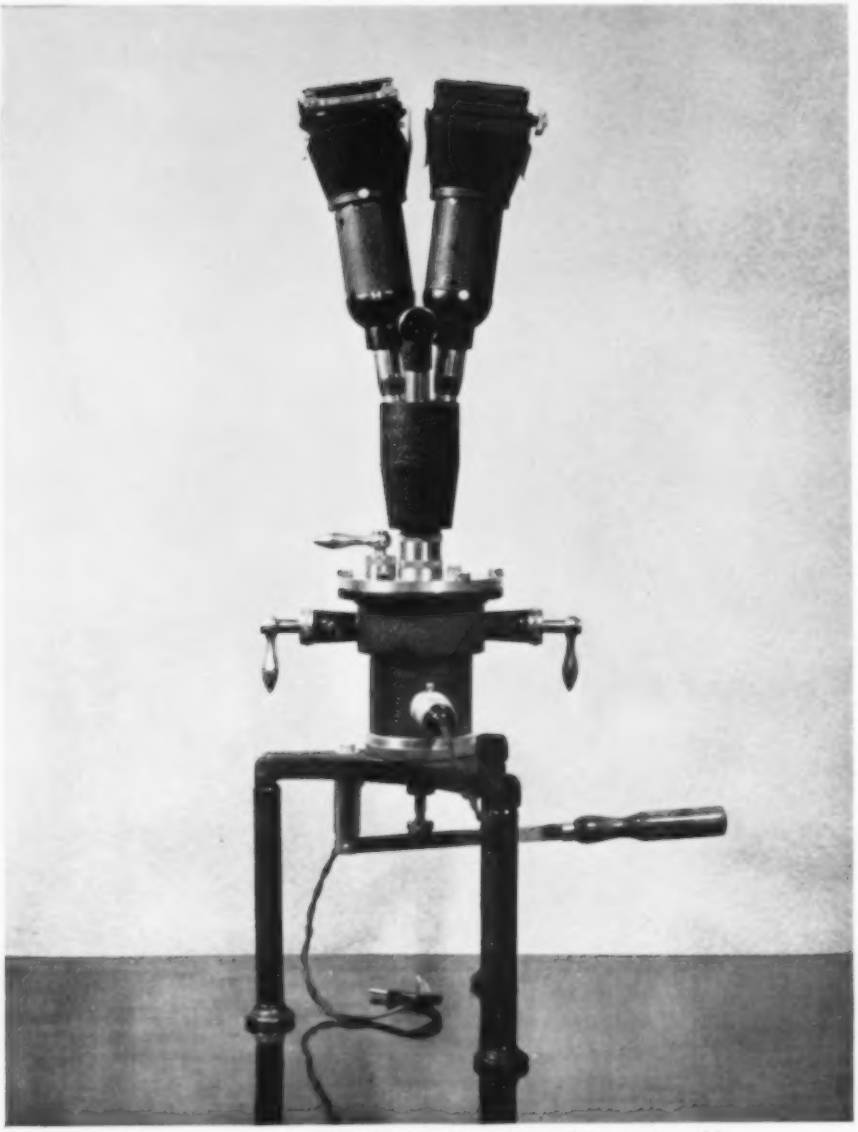

FIG. 1. Improved model of the condensation nucleus counter with stereo-photomicrographic recording.

VOL
1
1958/

determined in natural clouds and fog. A counter with the usual expansion ratio of 1·19, however, measures almost 11,000 nuclei. This discrepancy between counts of nuclei made with a conventional Aitken-type condensation nucleus counter of high expansion ratio and the number of droplets in clouds and fog is well known. For

TABLE 1. COUNTS OF CONDENSATION NUCLEI WITH A LARGE SCHOLZ COUNTER AT FOUR EXPANSION RATIOS (After L. FOITZIK)—AVERAGE OF FOUR INDIVIDUAL MEASUREMENTS AT LINDENBERG IN 1950

Expansion Ratio	1·19	1·12	1·05	1·02
Supersaturation (%)	300	200	140	110
April 17	8152	5885	4142	352
April 28	13,782	8190	5808	280
May 9	10,610	8065	5115	310

many applications to meteorology a set of nucleus counts at various expansion ratios would be of great interest.

The frequency distribution of counts which is of importance for assessing the reliability of nucleus counts has been investigated by SCRASE (1935) and POLLAK (1954). The first showers recorded on photograms have been used by POLLAK to test the hypothesis that the frequency distribution of counts can be adequately described by Poisson's exponential function. His results lead us to believe that there is no reason for abandoning the hypothesis that the counts of nuclei follow the Poisson distribution, or to look for another kind of distribution. Discrepancies between observed and expected frequencies may be attributed to chance.

VOL.
1
58/9

The only *relative* condensation nucleus counter which has been developed to a very high degree of accuracy and dependability and now used over the whole world, is the photo-electric nucleus counter based on a suggestion of POLLAK. It permits *individual* measurements of the concentration of condensation nuclei of high accuracy. Models of nucleus counters, designed to measure photo-electrically the decrease in intensity of a beam of light which has passed one or more times through an artificially produced fog, are described by L. W. POLLAK and W. A. MORGAN in a paper "On various photo-electric nucleus counters" on the files in the Irish Meteorological Service. They constructed early in 1490—as it happened in a garage at Foynes, Co. Limerick, from parts procured at Woolworth's or brought to Ireland by POLLAK—two primitive models, the "Direct Beam Photo-electric Nucleus Counter" and the "Multiflex Photo-electric Nucleus Counter", using the methods employed by POLLAK for measuring turbidity some years previously. The latter counter was intended for low nucleus concentrations such as would be encountered e.g. in aeroplane ascents. The calibration of an early model of the photo-electric condensation nucleus counter was carried out by NOLAN and POLLAK (1946).

The photo-electric counter consists of a vertical tube approx. 60 cm long (fog-tube) lined with damp ceramics and sealed hermetically on both ends by electrically heated glass plates. On the top there is an illuminator the light source of which produces through an optical system a parallel beam of light. At the bottom is a photo-cell. Air containing the nuclei under investigation is drawn or blown through the fog-tube for a time sufficiently long to ensure that the previous content is completely removed. Pure (filtered) air is pumped into the counter until a selected over-pressure is reached. After about one minute, so as to allow the air to become saturated with water vapour

and to lose heat of compression, the photo-current (I_0) is measured and the pressure is released. The sudden expansion cools the moist air and a fog is formed on the nuclei and the galvanometer reading drops to a new value (I). The extinction

$$E = 100(I_0 - I)/I_0$$

and the concentration of nuclei has been experimentally determined (NOLAN and POLLAK, 1946) by reference to an Aitken Pocket Counter. Thus, the absolute values of concentration measurements with the photo-electric counter at present are of the same accuracy as this Aitken counter; a re-calibration with the improved model of the recording stereo-photomicrographic counter just being undertaken will give considerably greater absolute accuracy. Where relative concentration determinations as e.g. in diffusion experiments are required, the photo-electric counter gives a high order of accuracy.

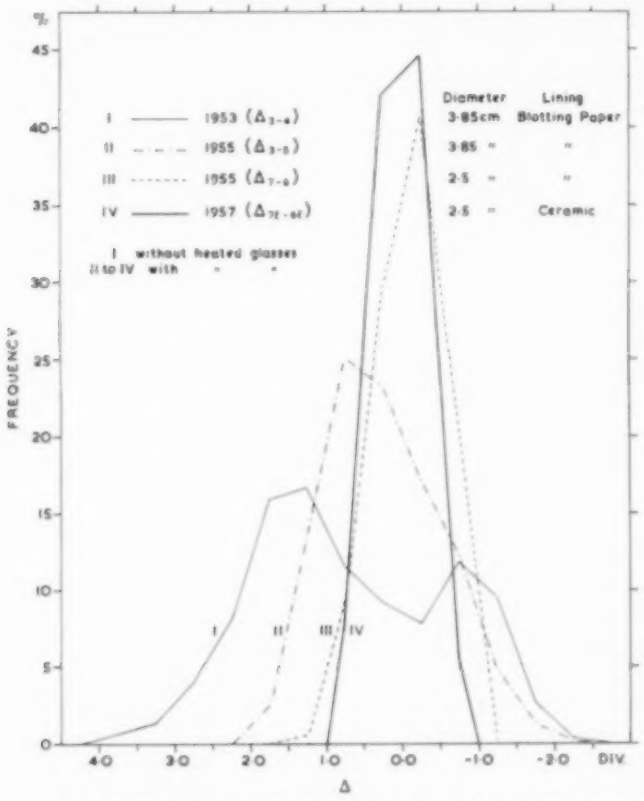

FIG. 2. Frequency of differences (Δ) between pairs of identical photo-electric condensation nucleus counters during the development of the counter.

Fig. 2 shows the frequency of differences (Δ) of *individual* readings between pairs of identical photo-electric counters during the period of development of the counter from 1953 to 1957 (POLLAK and METNIEKS, 1957c). It can be seen that the greatest improvements were achieved by the introduction of electrically heated sealing glasses,

the reduction of the fog-tube diameter (air-column diameter 2·5 cm) and the replacement of the blotting-paper lining by one of ceramics. Two counters Model 1957 agree in 72 per cent of all comparisons within 0·3 per cent of the maximum scale reading and in the majority of cases better. This is equivalent to a difference of 3 per cent in nucleus concentration or considerably less depending on the concentration measured. In 87 per cent of comparisons the corresponding figures are: 0·5 per cent of the maximum scale reading or 5 per cent in nucleus concentration. A difference of 1 per cent maximum scale reading has never been observed. The differences are due chiefly to random errors in the setting of the initial readings I_0 of the microammeters and also to the personal equation of the two observers carrying out the comparisons; the differences are considerably reduced when with very low concentrations (less than 200 nuclei/cm^3) a compensating circuit is used (POLLAK and METNIEKS, 1957b).

To produce a counter of this high accuracy and dependability which is truly leak-proof, the following principles have to be observed: greatest rigidity of the whole construction, air column diameter about 2·5 cm, ceramic lining, O–ring sealing and vacuum taps, well-collimated and centred light-beam with such a narrowed cross-section that the lining of the walls is not struck, uniform illumination of the whole sensitive surface of the photo-cell (leaving a dark annular ring around it), heated conducting sealing glass plates and durable photo-cells.

A modification of the photo-electric nucleus counter in which the direct light-beam of the previous construction is replaced by one bent at right angles with the aid of a prism, thus permitting easy access to the photo-cell, now accommodated on the *face* of the bottom part of the counter, is described by POLLAK and METNIEKS (1957b). In addition, in this model the 12 screws used hitherto for sealing the fog-tube on top and bottom were replaced by six quick-action toggle clips in order to speed up dismantling and re-assembling the counter or when carrying out certain experiments e.g. determining the droplet size of the cloud in the fog-tube.

The photo-electric nucleus counter, essentially as described above, is being used by VERZÁR (1953) in his automatic nucleus counter. Certain modifications (horizontal arrangement of the fog-tube, removal of the lining and the introduction of a humidifier in front of the fog-tube), however, which have been made, I consider rather unfortunate. Exact copies of the Irish photo-electric nucleus counter in vertical arrangement with very costly electronic pen and ink recorders are successfully employed for industrial purposes in the laboratories of the General Electric Company in Schenectady (U.S.A.).

The variation of the initial setting I_0 of the galvanometer pointer when pure air or air containing only few nuclei is adiabatically expanded in the fog-tube has been investigated (POLLAK and METNIEKS, 1957d) and methods for adjusting the collimated light in the illuminator of the counter described which eliminate the effect of this " scintillation " seriously interfering with the measurements at very low concentrations e.g. in aeroplane ascents or in the clean air over the ice of the polar regions.

The relationship between extinction and the length of the light path in the fog-tube was investigated for a fog-tube length of 117·5 cm and the effect of the heating of the sealing glasses and of the distance of the photo-cell from the bottom sealing glass studied (POLLAK and METNIEKS, 1957c).

The effect on the measurements with the photo-electric counter of isothermal distillation, shrinking of the droplets by evaporation without recondensation of the

liberated water vapour, coagulation and differential settling of the fog droplets which take place in the fog-tube were numerically examined (POLLAK and METNIEKS, 1959). The results of these computations explain the occurrence of a small additional extinction (" creep ") in the first seconds after the fog has formed in a fog-tube of more than say 3·5 cm air-column diameter. Since, due to the accelerated heat-flow from the walls in fog-tubes of diameters 2·5 cm and less " creep " has never been observed, fog-tubes of 2·5 cm diameter are now adopted as standard. Narrower fog-tubes are not recommended on account of the considerable diffusion losses during the time lapse between expansion and taking the sample.

The size of the fog droplets in the cloud chamber of the photo-electric counter was determined by collecting the falling droplets on gelatine coated slides dyed with Naphtol Green B (POLLAK and METNIEKS, 1959). It was found that the radius of the droplets increases from 1·44μ at 67·4 per cent extinction (42,400 nuclei/cm^3) to 6·30μ at 15·6 per cent (858 nuclei/cm^3). This wide range of droplet size shows also the superiority of determining the nucleus concentration photo-electrically since the extinction produced by droplets of all sizes is measured.

2. APPLICATIONS OF THE COUNTING RESULTS

The great accuracy and dependability of the photo-electric counter together with its feature enabling almost instantaneous values to be obtained, made possible investigations previously quite out of the question, and the carrying out in as many hours of experiments which with the older types of absolute nucleus counters would have and have taken months.

Apart from measuring directly the number of nuclei/cm^3 and their charged and uncharged portion, the following properties of condensation nuclei can be deduced from concentration measurements: decay (coagulation and sedimentation) in closed vessels, diffusion coefficient (size), mass, density, and the size of droplets formed on nuclei in fog.

One of the *oldest applications* of counting nuclei is the *compilation of climatological statistics of nucleus concentrations and their relationship to meteorological elements.* These statistics are based altogether on certainly millions of individual measurements over the whole globe, over land and sea, on mountain peaks, in manned balloons and aeroplanes. The first modern statistics using measurements made with a photo-electric nucleus counter at the School of Cosmic Physics in Dublin (5, Merrion Square) was published by NOLAN and TEDDE (1950). It deals not only with the concentration of nuclei and their correlation with wind and relative humidity but also with the size and charge-distribution of the nuclei.

POLLAK and MURPHY (1952) equipped a motor van with photo-electric nucleus counters and accessories and carried out extensive nucleus concentration measurements throughout Ireland. One noteworthy result deduced from their observations made with this mobile laboratory in polar air, is the uniformity of nucleus distribution over the whole of Ireland if contamination from nuclei produced by human activity is avoided. Another conspicuous feature, which was common to three consecutive days at the Atlantic coast when there were passing showers in the morning, clearing afterwards and with wind from the sea throughout, is the enormous fluctuation in the numbers of nuclei within a matter of minutes and from concentrations of about 100 nuclei/cm^3 up to as high as 206,000/cm^3 within $\frac{3}{4}$ hr.

The *droplet size of fog and clouds* can be deduced from extinction measurements for two wavelengths. POLLAK and METNIEKS (1959) used a red and a blue monochromatic interference filter in two identical photo-electric counters of 2·5 cm fog-tube diameter in parallel in order to determine also in this way the size of the droplets formed in the fog-tube of a photo-electric counter. The radius of the droplets obtained by the optical method varies from 1·81 to 3·19μ when the extinction decreases from 86 per cent (148,560 nuclei/cm^3) to 56 per cent (16,560 nuclei/cm^3).

The introduction into condensation nuclei research of *large gasometers consisting of rubber radiosonde balloons* (POLLAK and MURPHY, 1953) made it possible to study among other properties the coagulation, sedimentation and variation in size of e.g. room air nuclei without the serious disadvantages inherent in small vessels. This rubber gas holder, containing easily up to 8000 l. when a 500 g radiosonde balloon is used, can be inflated with filtered air, room air, or outdoor air and the nuclei to be investigated can be produced by a heated spiral of wire mounted in the centre of the balloon. The nuclei, decaying in the balloon, supply a wide range of nucleus concentrations.

The rate of *disappearance of condensation nuclei in a closed vessel* can be described according to NOLAN (1933 and 1941) by the differential equation

$$dZ/dt = -\gamma Z^2 - \lambda Z \qquad (1)$$

where Z denotes the number of nuclei per cm^3 and dZ/dt is the rate of disappearance of condensation nuclei in the closed vessel. The γZ^2 term represents loss by coagulation, the λZ term expresses loss by diffusion to the walls of the container and by sedimentation. The term γZ^2 is dominant when Z is large. The linear term becomes important when Z is smaller than approx. 5000 nuclei/cm^3, since the ratio λ/γ is of the order of 1000.

The coefficients γ and λ were treated (NOLAN, 1941) as constants for the integration of equation (1). That the coefficient γ during the decay is not a constant follows from Smoluchowski's theory and has been known for some time. Regarding λ it was shown (NOLAN, 1933) that its value depends on the size of the vessel and NOLAN (1941) suggested that its component λ_d due to diffusion varies with the ratio of area to volume of the container. Only during recent investigations (FÜRTH, 1955; POLLAK and O'CONNOR, 1955), however, did it come to light that λ even for the same vessel is not a constant but depends on time.

Using the method of least squares, solutions of simultaneous values of γ and λ were obtained for room air decaying in a large balloon gasometer (POLLAK *et al.*, 1954). The determination of γ and λ by this method leads to overall values of γ and λ for the whole time of the experiment when they are assumed constant in the calculation. If the calculation is carried out for parts of the whole duration of the experiment it is possible to study the variation e.g. of γ, the coagulation coefficient. The average values in the decay law of room air nuclei in a large rubber gasometer are $\gamma = 1{\cdot}75 \cdot 10^{-9}$ cm^3 sec^{-1} and $\lambda = 1{\cdot}69 \cdot 10^{-6}$ sec^{-1}.

Determination of the diffusion coefficient and size of nuclei

There are two experimental methods known for determining the diffusion coefficient of nuclei which I have named the static and dynamic methods.

(*a*) *Static method.* The theory of this method has—on my request—been developed

by FÜRTH (1955). One of the two procedures given by FÜRTH's theory uses the initial concentration Z_o and the concentration Z_t after the decay of nuclei in a cylindrical container over a period of t sec.

The static method is indispensable in all cases where the concentration of the nuclei changes rapidly as e.g. during aeroplane flights. This method requires only the filling of the fog-tube of two identical photo-electric nucleus counters with the air containing the nuclei the size of which has to be determined, to measure the number of the nuclei in one of the counters immediately after sampling, giving Z_o, and to measure after a certain time t, say 30 or 60 sec, the number of nuclei in the other counter Z_t.

Assuming a sufficiently small duration t of the decay experiment the diffusion coefficient D is obtained from

$$Z_t/Z_0 = g\left(\frac{Dt}{R^2}\right) \tag{2}$$

where the function g is defined by

$$g(\xi) = 4 \sum_{i=1}^{\infty} y_i^{-2} \exp(-y_i^2 \xi), \tag{3}$$

y_i are the positive roots of the Bessel function of order zero, thus $J_o(y_i) = 0$ and R is the radius of the effective cylindrical vessel; in the case of the fog-tube being used, therefore, the radius of the air column.

Based on our tests of the static method (POLLAK *et al.*, 1956), FÜRTH extended equation (2) in order to take into account the thin layer of air adjacent to the walls of the cylindrical decay vessel assumed to remain almost stationary during the filling process.

The equation

$$g\left(\frac{Dt}{R^2}\right) = \frac{Z_t}{Z_o}\left(1 - \frac{2l}{R}\right) \tag{4}$$

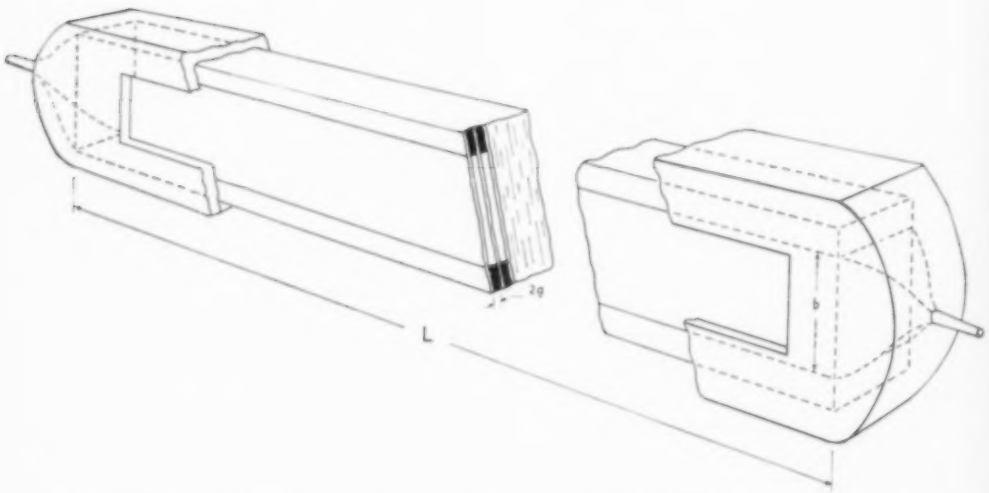

FIG. 3. Diagram of diffusion apparatus for dynamic method (School of Cosmic Physics, Dublin).

where l denotes the thickness of the boundary layer, replaces equation (2). From our measurements FÜRTH estimated the thickness of the layer l at about 1·5 mm.

(*b*) *Dynamic method.* This method of determining the diffusion coefficient of nuclei was devised by the late J. J. NOLAN and his pupil V. GUERRINI.

The nuclei are passed through a box containing a number of airtight rectangular channels arranged in parallel. A diagram of an improved diffusion apparatus constructed in the workshop of my laboratory is shown in Fig. 3. Regarding details of the construction the reader is asked to consult POLLAK *et al.* (1957). As can be seen from the figure, the narrow channels are arranged vertically when the diffusion coefficient alone is to be determined.

The theory of the dynamic method (NOLAN and GUERRINI, 1935; NOLAN *et al.*, 1938) assumes that the air-flow is parallel to the length of the channel and that there is only one diffusion coefficient of the nuclei. The nucleus concentration Z at the entrance of the channel and the concentration Z_v at its exit are measured. The suffix v in Z_v stands for " vertical " denoting that the long dimension of the cross-section of the channels is in a vertical position. In this arrangement the loss of nuclei by fall under gravity may be assumed negligible and to be due only to diffusion. The ratio of the concentrations (number of nuclei) Z_v/Z is related to the diffusion coefficient D of the nuclei, the volume of air q passing per second through each channel and the dimensions of the channel (L = length, b = height and $2a$ = width) by the following formula

$$Z_v/Z = 0{\cdot}9099 \exp(-x) + 0{\cdot}0531 \exp(-11{\cdot}4x) \tag{5}$$

where

$$x = 3{\cdot}77\, b\, L\, D\, a^{-3} q^{-1}. \tag{6}$$

If c is the number of channels in the diffusion apparatus, the volume of air passing per second through the diffusion apparatus $Q = cq$.

The total air-flow Q through the diffusion box is usually adjusted in practice so that the ratio Z_v/Z has a value of between 0·7 and 0·2 and the duration of a complete experiment is not unduly long.

We investigated (POLLAK *et al.*, 1956) the *effect of varying the air-flow* on the results obtained by the dynamic method. A regular and systematic increase of the diffusion coefficient with increase of air-flow was discovered. Within the range of 1 to 4 l./min air-flow a change by 1 l./min alters the diffusion coefficient by roughly 12 per cent. Since for technical considerations during one experiment adjustments of the air-flow by 2 l./min were not uncommon up to now, the diffusion coefficient may be wrong by 25 per cent of its value for this reason alone, a fact apparently overlooked hitherto.

Whereas THOMAS (1955) states " The cause for the discrepancy, i.e. higher diffusion constants with higher flow rates, has not been determined ", POLLAK and METNIEKS (1957a) showed that the marked influence of the air-flow on the value of the diffusion coefficient as determined by the dynamic method can be fully explained when *heterogeneity* of the condensation nuclei in the aerosol is assumed. They gave a theory of the dynamic method for heterogeneous aerosols and developed procedures for resolving heterogeneous aerosols into their components using the dynamic method.

The size of the nuclei is computed from the diffusion coefficient using the well-

known Einstein equation modified for particles which are small compared with the mean free path of the molecules of the gas (NOLAN and TEDDE, 1950)

$$D = \frac{RT}{N} \cdot \frac{1+(\lambda/r)(A+Be^{-(cr/\lambda)})}{6\pi\eta r} \tag{7}$$

where λ is the mean free path and $A = 0{\cdot}864$, $B = 0{\cdot}290$ and $c = 1{\cdot}25$.

Mass of nuclei

If the diffusion box is arranged so that the long dimension of the cross-section of the narrow channels is in a horizontal position and, therefore, the sheets of flow are horizontal, both diffusion and fall under gravity contribute to the loss of nuclei.

From the fraction k of nuclei lost in the diffusion battery when horizontally arranged the velocity of their fall under gravity

$$V_g = \frac{Q \cdot k}{zb} \tag{8}$$

can be calculated where Q is the volume of air passing through per second, L the length and b the breadth of the rectangular channel.

Then the mass of the nuclei is found from the equation

$$m = \frac{V_g}{D} \cdot \frac{RT}{Ng} \tag{9}$$

where D is the diffusion coefficient as determined by the dynamic method when the channels of the diffusion apparatus are arranged vertically, R is the gas constant per gramme molecule, T the absolute temperature, and N the number of molecules per gramme molecule.

Taking e.g. $D = 12 \cdot 10^{-6}$ and $V_g = 16 \cdot 10^{-5}$ NOLAN *et al.* (1938) find for the mass of the corresponding nucleus

$$m = \frac{16 \cdot 10^{-5}}{12 \cdot 10^{-6}} \cdot \frac{831 \cdot 10^{5}}{6{\cdot}06 \cdot 10^{23}} \cdot \frac{288}{980} = 5{\cdot}4 \cdot 10^{-16}\ \text{g}.$$

Practical applications

The photo-electric precision nucleus counter as developed by POLLAK and a most interesting photo-electric instrument for counting nuclei and their size discrimination due to RICH (1957) are extensively used in the General Electric Company's General Engineering Laboratory in Schenectady (New York) and elsewhere.

Only now, as RICH points out, are engineers beginning to understand the techniques for particle measurement and their " benefits to mankind ranging from better air-conditioning equipment and control of air pollution in cities to development of better electric control devices."

It is not sufficient, however, to determine only the number of particles discharged into the air but also to measure in air pollution investigations the size (mass) of the pollutants.

Regarding the purely technical applications of the photo-electric nucleus counters see RICH (1957). RICH used e.g. the nucleus counters for measuring the arcing between electrical contacts and determined the degree of contact erosion. He was in this way able to find the best operating conditions for a specific type of contact.

Improvement in design or material as determined by nucleus counts is statistically more significant than a conventional life test. From such an investigation data were obtained that actually more than doubled the life of a contact.

Acknowledgement—I am indebted to Professor Dr. MARIO BOSSOLASCO, Editor of *Geofisica pura e applicata*, Milano for permission to reproduce the three figures accompanying this article from papers published or in course of publication in his journal.

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VOL.
1
58/9

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1
1958

Int. J. Air Poll. Pergamon Press 1959. Vol. 1, p. 307. Printed in Great Britain.

Notes and News

Conference on Air Pollution held in Japan

We have received summaries of several papers which were presented at a conference on air pollution held in Japan recently. Two were published in No. 3 of this Journal. Four others are summarized here.

Takeo Suzuki discussed the results of a survey made in the cities of Tokyo and Amagasaki. The daily cycle of pollution showed the usual features except that in Tokyo the evening maximum was higher than that of the morning. The weekly curve showed an increase from the Sunday minimum to a maximum on Fridays. The amount of dust in the atmosphere was found to vary inversely as U^n where U = wind speed and $n = 0{\cdot}56$.

A report of the Kinki District Research Committee described an intensive investigation, in which schools, colleges and various public authorities collaborated, into the distribution of pollution around Osaka and Amagasaki, important industrial areas, and in Kobe, Kyoto and Wakayama. For the most part quite high concentrations of SO_2 were observed in the manufacturing cities but in surrounding areas, e.g. 10–20 km from Osaka, the presence of SO_2 could not always be detected.

In Tokyo the concentration of dust in the air has been measured during summer and winter periods in a wide variety of places—outdoors, houses, factories, theatres, schools, and department stores. The results were communicated in a report by Komoda, Suenaga and Osada.

An investigation extending over a whole year into sulphur dioxide pollution in Kanagawa was described by Kanno and Fukui. The observations were subjected to a comprehensive analysis in terms of meteorological parameters, and hourly, monthly and seasonal means were worked out. Curves were drawn to show the daily cycle of pollution in cloudy, rainy and clear weather and also the variation of concentration with wind speed in each season and with lapse rate.

VOL.
1
958/9

Int. J. Air Poll. Pergamon Press 1959. Vol. 1, pp. 308–310. Printed in Great Britain.

Book Reviews

Appraisal of Air Pollution in Texas. Austin, Texas, U.S.A. Texas Department of Health, 1958. 107 pp., 17 figures, 41 tables.

THE growing concern with air pollution in the United States of America is reflected in both increased primary research in this field, such as the survey being conducted by the National Air Sampling Network of the United States Public Health Service, and in increasing state and local legislation aimed at its regulation. State laws relating directly to air pollution have been enacted by more than half the states and their scope ranges from the establishment of advisory committees to the formation of government bodies empowered to regulate pollution and organize comprehensive programmes of research.

In Texas there are no state laws or regulations pertaining specifically to air pollution although some municipalities have regulating ordinances. But even local activity is limited in geographical extent and adequacy and it was the need for both state and local programmes of research and control which occasioned this primary survey of the nature and extent of air pollution in Texas. The problem has been emphasized by the tremendous expansion of population and industry since 1940.

Precise measurements of air pollution in the state are very meagre and much of this report was based upon qualitative estimates and opinions obtained by interviews with well-informed individuals (usually the local health officers), questionnaires, and direct observation. Based upon this information, but closely restricted by its general nature, the report defines the current air pollution problems in Texas, discusses the factors having either a direct or indirect bearing on the production and dissemination of pollutants and makes recommendations for further research and legislation at both state and local levels.

The nature of the major pollutants differs markedly from those in Great Britain. More than 50 per cent of the fuel energy consumed in Texas is supplied by natural gas and much of the remainder by fuel oil, more than half of which is taken by vessels whose contribution to the overall pollution load of the coastal cities is considered to be small. In consequence, the state does not have the tremendous problems of smoke, fly-ash and sulphur dioxide commonly associated with coal and oil burning domestic and industrial premises. Of more importance in Texas is the pollution from motor vehicles, cotton-ginning and other manufacturing industries. The full significance of cotton-ginning is realized when one considers that almost a quarter of the total state cropland harvested was in cotton and modern processes have greatly increased the volume of lint and dust discharged into the air. Up to 1000 pounds of waste may be produced from each bale of cotton ginned.

Sources of pollution are considered both systematically and regionally (bearing in mind relevant meteorological, climatological and topographical controls) but, from the available data, no more than general estimates can be made of their relative importance.

This survey adds little, if anything, to the general theory of air pollution and the lack of precise data limits its value as a factual descriptive account. It was produced by the state authorities as a first step to more detailed work and possible legislation. Outside Texas, its techniques could usefully be employed in a similar context or in those areas where instrumental measures are impossible or unnecessary.

T. J. CHANDLER

Air Pollution Measurements of the National Air Sampling Network. Analysis of Suspended Particulate Samples Collected 1953–1957.

U.S. Department of Health, Education and Welfare. Public Health Service. Bureau of State Services. Division of Sanitary Engineering Services. Robert A. Taft Sanitary Engineering Center, Cincinnati 26, Ohio. Public Health Service Publication No. 637. United States Government Printing Office, Washington, D.C., 1958. $2.00.

THE report presents data on suspended particulate matter in the air over the United States and is the result of the first five years of the U.S. Public Health Services National Sampling Network. One of

the aims of this sampling is the establishment of trends and patterns of air pollution in the United States.

A chapter devoted to the chemical procedures and statistical analyses furnishes the necessary technical information for the establishment of similar or identical sampling stations by other agencies. From 17 stations in 1953 the program has expanded to the operation of about 110 urban and 51 nonurban stations in all 49 states, the District of Columbia, the Territory of Hawaii and the Commonwealth of Puerto Rico.

The report deals with suspended particulate matter consisting of smoke, dust and fumes, solids and droplets of inorganic and organic nature. The organic material collected on specially prepared filter paper is extracted with organic solvents. These fractions contain substances such as cancer producing polynuclear aromatics and other substances which may cause irritation of animal tissue. The inorganic constituents determined are: chlorides, fluorides, sulfates, nitrates, metals and radioactive material. The samples are obtained with a high volume air sampler operated for 24 hr using an 8 in. × 10 in. glass fiber filter capable of removing practically 100 per cent of all particulates 0·3 μ or greater in diameter. The flow rate is about 40–50 ft^3/min.

Monthly and frequency distribution tables have been prepared for the following atmospheric pollutants: suspended particulates, acetone soluble organic matter, radioactivity, chlorides, fluorides, nitrates, sulfates, barium, bismuth, cadmium, copper, chromium, iron, lead, magnesium, manganese, nickel, potassium, sodium, strontium, tin, titanium, vanadium and zinc. The data for antimony, arsenic, beryllium, cobalt, molybdenum and silver are presented in separate tables.

The report represents a tremendous amount of data which need a great deal of analytical study before their real value can be properly evaluated. An attempt to cover the total area of the United States adequately is prohibitive in cost and information on local pollution levels will largely have to come from local government.

The most useful information obtained from the national air sampling program may well be in the collection of data not affected by local pollution. Determination of trends in carbon dioxide concentration are of great interest to those studying changes in our atmosphere and consequent heat balance. The operation of stations in urban areas will make a definite, valuable educational contribution to the awareness of the problem of clean air.

The trends of atmospheric changes in the atmosphere will be slow and many years will go by before conclusions can be statistically valid. It is therefore of great importance that the methods used and the substances to be determined should be standardized, and the number of stations and their locations chosen so that the future of this monumental task will be assured.

A. J. Haagen-Smit

VOL.
1
958/9

R. S. Scorer: **Filmstrips (in colour) and Lecture Notes on Air Pollution. A: Nature, production and effects of air pollution. B: Dispersion and accumulation of air pollution: behaviour and appearance of smoke.** Produced by Diana Wyllie Ltd., London S.W. 1. 32 frames each strip, pictures 35 × 24 mm, lecture notes for both strips, 29 pp., £4 complete.

These excellent colour filmstrips are a valuable source of illustrations for lecturers on atmospheric pollution. They may be cut up and used as individual slides if preferred. Though primarily aimed at a non-technical public, there is much of interest to experts as well. Sir Hugh Beaver contributes a thoughtful foreword.

The sources, behaviour and effects of air pollution are well covered, often in a striking manner. It would, however, be desirable to have some pictures showing what improvements can be made by tackling the problem. The filmstrips tell a doleful tale of pollution, emitted from millions of sources, perhaps accumulated by the process of nature, doing untold harm to human beings, cow's teeth, vegetation and masonry. This depressing story would be more stimulating and useful if some pictures showed the reduction in pollution possible following appropriate action. Perhaps further filmstrips will be produced showing such improvements.

Bearing in mind the fact that the filmstrips are primarily aimed at the non-technical public, there are perhaps too many detailed descriptions of industrial processes, but the lecturer could avoid boring his audience by selective omissions. Sub-titles on each exposure would reduce mind wandering and focus attention on the spoken commentary, and indeed assist the lecturer.

The diagrams at the beginning and end are difficult even for the technical mind to interpret. Diagrams B30 " assigning the blame " and B31 " the cost of pollution in Britain " are particularly obscure and, as they are most important, it is strongly recommended that they be recast, possibly as histograms.

J. F. DOWLER

PAPERS ACCEPTED FOR PUBLICATION

E. L. DEACON: The problem of atmospheric diffusion.

R. TRAPPENBERG: Die Ausbreitung von Staub und Gas nach Sutton.

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VOL
1
1958/

VOL.
1
58/9

END OF VOL.